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A new class of sorbents for the selective removal of arsenic(V) and selenium(IV) oxy-anions

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A NEW CLASS OF SORBENTS FOR THE SELECTIVE REMOVAL OF ARSENIC(V) AND SELENIUM(IV) OXY-ANIONS

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Table of Contents

List of Figures

List of Tables

Abstract

Groundwater contamination by trace concentrations of arsenic(V) and selenium(IV) is widespread. This poses a serious problem since arsenic and selenium are toxic and are on the USEPA's list of priority pollutants. As groundwater is increasingly becoming a source of potable water, treatment for the removal of arsenic(V) and selenium(IV) oxy-anions, present at low concentrations, needs to be practised.

Selective removal of trace concentrations of arsenic(V) and selenium(IV), in the presence of high sulfate and chloride concentrations, is a challenging separation problem. Conventional treatment techniques, such as coagulation and fixed-bed sorption using strong base anion-exchangers or activated alumina are not effective in this respect.

In this study, synthetic chelating polymers with pyridine based functionalities were used in their copper loaded forms to selectively remove selenium(IV) and arsenic(V) oxy-anions. Sulfide removal by the sorbents was also studied. These tailored sorbents offered over an order of magnitude greater affinity for arsenate and selenite, compared to strong-base anion exchangers.

The high selectivity of these resins toward trace concentrations of arsenate, selenite and sulfide anions, even in the presence of high sulfate and chloride concentrations, could be attributed to anion exchange accompanied by Lewis acid-base interaction. The high uptake of these species is related to the extremely low solubility products of their copper(II) compounds. The sorbents could be regenerated very efficiently with ammonia, thus enabling their repeated use over a number of cycles.

In summary, conventional sorbents such as activated carbon, activated alumina and strong-base anion exchangers cannot selectively remove arsenic(V)

and selenium(IV) oxy-anions in the presence of competing sulfate and chloride anions. This study identifies a new class of sorbents which can overcome this problem.

The effects of process variables such as pH, nature and concentration of competing ions, and the composition of functional groups on arsenic(V) and selenium(IV) uptake were investigated. A mechanistic model based on anion exchange accompanied by Lewis acid-base interaction can explain the effects of these variables satisfactorily.

Chapter 1
INTRODUCTION

1.1 TOXIC SUBSTANCES

Selenium and arsenic are toxic metalloids and are included in the USEPA's list of priority pollutants. Groundwater contamination by arsenic and selenium is fairly widespread. This poses a serious problem as groundwater is increasingly being used as a source of potable water.

The major source of selenium in the environment is the weathering of rocks and soils but human activities also contribute about 3,500 metric tons per year[1]. Selenium is also acutely toxic to aquatic invertebrates and fishes. It is associated with uranium mining and has been reported in groundwaters, in mining areas, in Colorado, Arizona and New Mexico[2].

Arsenic is a common constituent of coals. Acid mine drainage in the Rocky mountains has been found to contain 6.0 - 22.0 mg/L of soluble arsenic[3]. Gold ore extraction wastes contain soluble arsenic at the level of 132 mg/L[4]. Consumption of water containing arsenic causes blackfoot disease. High content of arsenic (0.6 - 2.0 mg/L) in the drinking water in some parts of Taiwan is believed to be the cause of black-foot disease[5]. Severe poisoning is caused by the intake of 100 mg of arsenic. Consumption of water containing more than 0.2 mg/L of arsenic, over a prolonged period can also cause chronic poisoning symptoms.

Selenium and arsenic are believed to be potential carcinogens although no data has been obtained in support of their carcinogenicity. However, both arsenic and selenium have adverse and beneficial effects depending on the amount ingested. The maximum no-observed-adverse-effect level for arsenic in water is less than 100 ug/L and for selenium is at least 100 ug/L though it could

be as high as 500 ug/L[2].

Arsenic and selenium occur in industrial process solutions and effluents posing a serious pollution hazard. Electroplating wastes contain 23 mg/Kg of selenium and incinerated mixed municipal waste contains 53 mg/Kg of selenium [6]. Selenium is also used in stainless steel production and the glass and ceramic industry. Electrolytic refining of copper is one of the best characterised industrial sources of selenium wastewater. Arsenic and arsenical compounds have also been reported in wastewaters of the metallurgical industry and of glassware and ceramic production. Tannery wastes also contain arsenic in appreciable quantities. Dye, pesticide and herbicide manufacture also leads to the production of arsenic wastes. Deep-well waters in the desert areas of the southwest United States contain arsenic at levels exceeding 0.1 mg/L[7].

In addition to arsenic and selenium, hydrogen sulfide is another contaminant commonly found in groundwaters. It is not toxic but is undesirable in drinking water due to its odor. Sulfates occur in most groundwater environments to form objectionable concentrations of hydrogen sulfide gas. Shallow wells are susceptible to surface water contamination, which may have a high concentration of organics. Thus shallow wells are prone to the problem of hydrogen sulfide formation - leading to odor problems[8]. Sulfides are formed by the anaerobic reduction of sulfates and organic matter into sulfides and bisulfides. Sulfides also promote the growth of filamentous sulfur bacteria, leading to a general degradation of water quality.

1.2 EXSISTING GUIDELINES AND STANDARDS

The U.S. Environmental Protection Agency has established a maximum contaminant level (MCL) of 0.01 mg/L for selenium and 0.05 mg/L for arsenic as part of the National Interim Primary Drinking Water Regulations (NIPDWR). Wastes leaching selenium in excess of 1 mg/L during the Extraction Procedure toxicity test are classified as hazardous. Using the same proportioning factor as for selenium, the level of arsenic in leachate from the EP toxicity test is set at 5 mg/L. Taste and odor standards exist for sulfide but it is not toxic to humans. The recommended levels of sulfide, in water, are species specific. It has been reported in literature that 0.4 mg/L of H_2S is toxic to fish.

1.3 AQUEOUS CHEMISTRY

Prior to discussing the treatment techniques employed to remove arsenic, selenium and sulfide it is important to understand the aqueous chemistry of each species. Arsenic can occur in four oxidation states in water (+5, +3, 0, -3). It exists as an anion with acid characteristics in only the trivalent (arsenite) and pentavalent (arsenate) forms. Arsenate is less toxic than arsenite[9]. Trivalent arsenic is considered to be 3 to 20 times as toxic as pentavalent arsenic[10]. Figure 1-1 is the pE-pH diagram for arsenic in a system including oxygen and water[11].

This diagram indicates the predominant species under various oxidation-reduction conditions and pH values. Arsenite is more likely to be found in anaerobic groundwaters and arsenate in aerobic surface waters. The concentration of arsenic in groundwaters ranges from a few ug/L to 8 mg/L. Data on the speciation of arsenic in groundwaters is limited. However, it is known that the valence state of arsenic in groundwater varies with the location [10]. The oxyanions of arsenic in the +5 state are $H_2AsO_4^-$, $HAsO_4^-$ and AsO_4^{3-}.

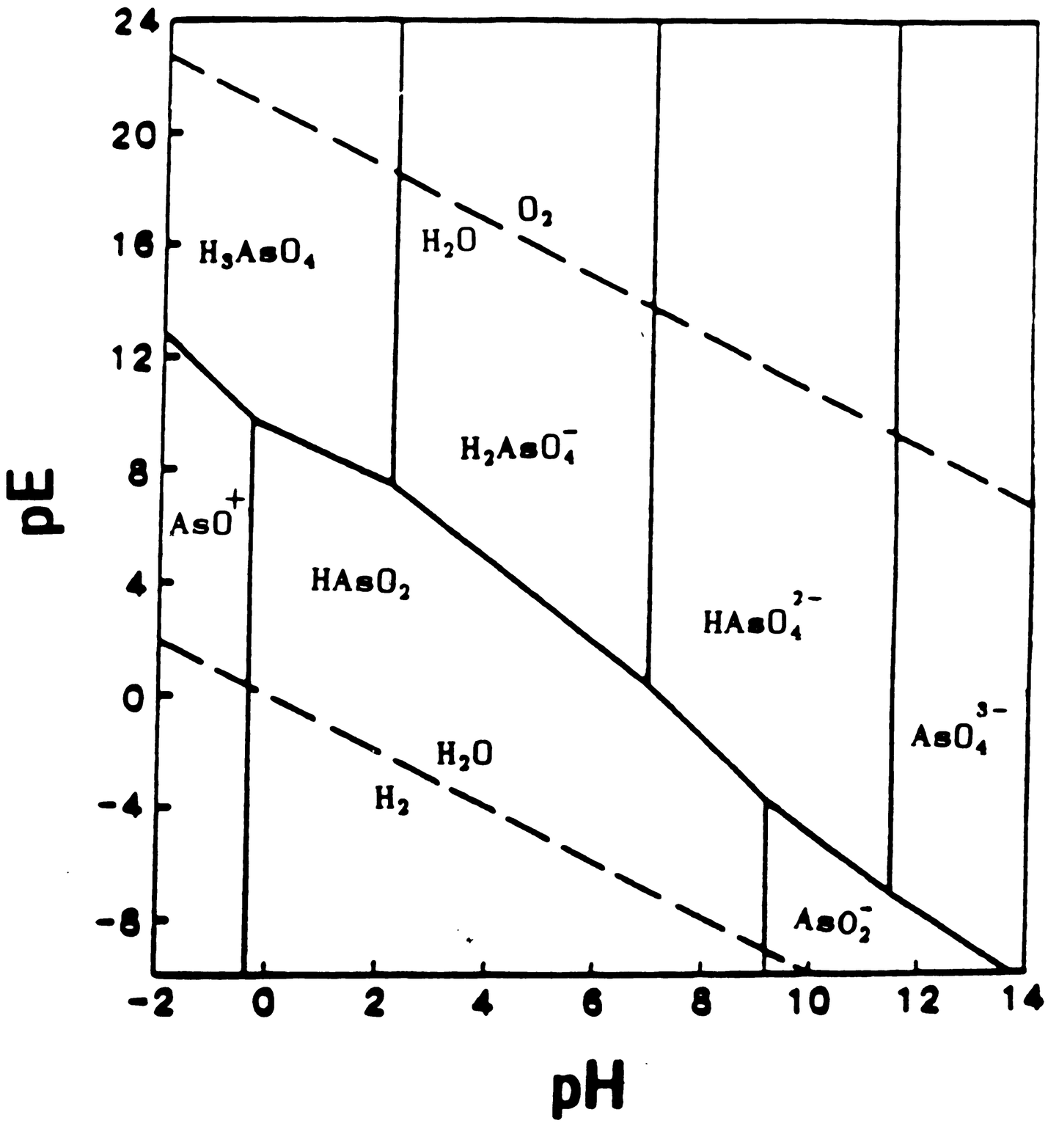


Figure 1-1: pE-pH Diagram For Arsenic

The speciation would depend on the pH of the water relative to the three pK values of H_3AsO_4 - pK_1=2.5; pK_2=6.77; pK_3=11.6[12]. In the pH range of 4-10, the the predominant forms of arsenate species are $H_2AsO_4^-$ and $HAsO_4^{2-}$. The rate of oxidation of arsenic(III) to arsenic(V) is very slow at neutral pH values, but proceeds measurably in strong acid or alkaline solutions[13]. The oxidation state of arsenic has a significant effect upon the efficiency of some treatment techniques employed for arsenic removal.

The two predominant aqueous species(oxy-anions) of selenium are selenium(IV) or selenite and selenium(VI) or selenate. Like arsenic, selenium occurs as an anion and has acid characteristics. The oxy-anion of selenium in the +6 state is SeO_4^{2-}, which is very similar to SO_4^{2-}. The oxy-anions of selenium in the +4 state are $HSeO_3^-$(biselenite) and SeO_3^{2-}(selenite). The speciation would depend on the pH of water relative to the two pK values of H_2SeO_3 - pK_1=2.4; pK_2=7.9. Figure 1-2 is the pE-pH diagram for selenium, adapted from[11].

In well-aerated surface waters containing selenium, SeO_4^{2-} would be the predominant species. $HSeO_3^-$ would be present to a greater degree in waters with reducing conditions. The selenite ion appears to be the most common form of selenium in wastewaters, except for solid forms of the selenide resulting from mining, ore milling and pigment and dye manufacture.

Hydrogen sulfide predominates at pH less than 7, the bisulfide ion dominates between pH 7 and 9.5 and the sulfide ion is predominant above pH 9.5. Figure 1-3 shows the speciation of hydrogen sulfide at various pH values[12]. Figure 1-4 is the pE-pH diagram for the sulfate - sulfide system.

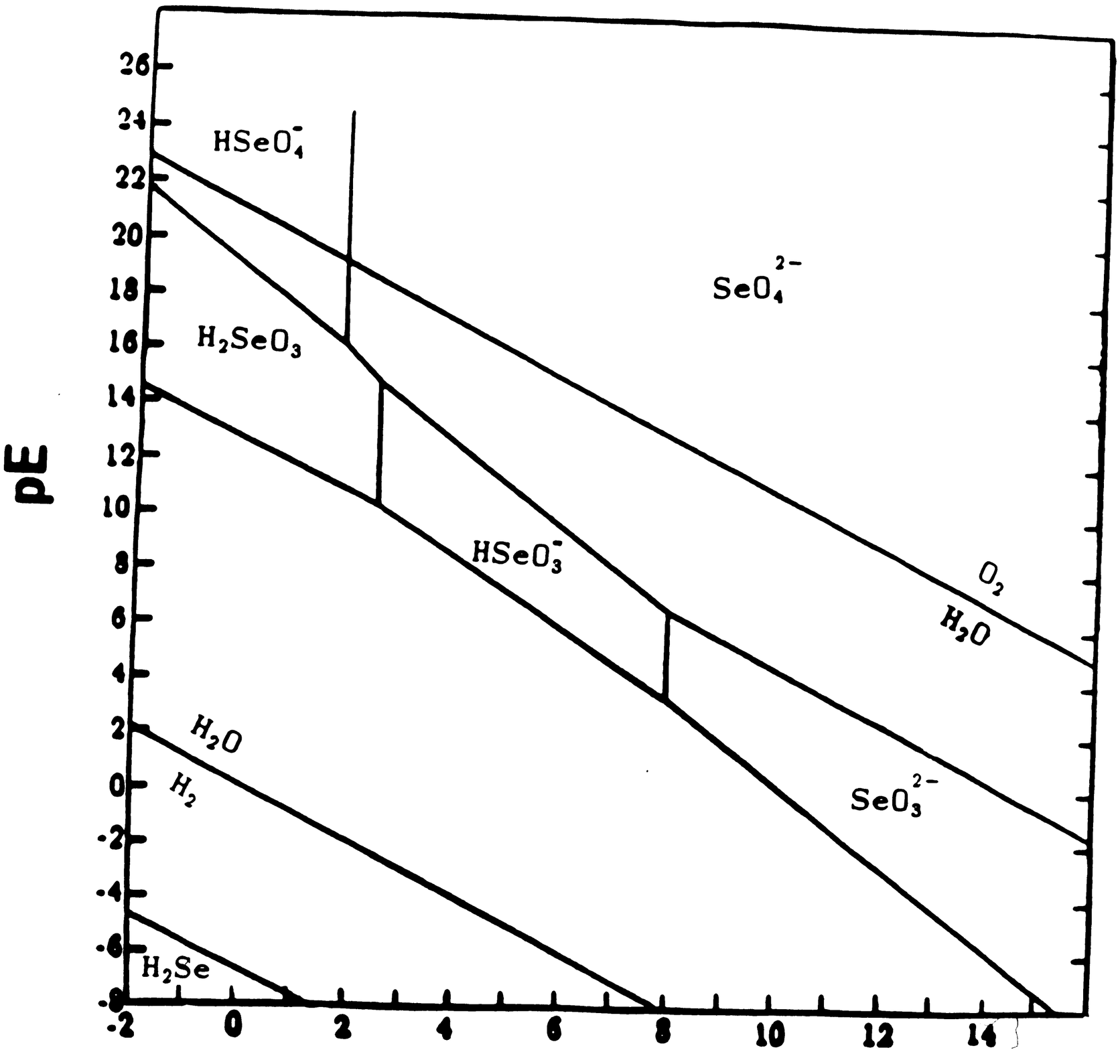


Figure 1-2: pE-pH Diagram For Selenium

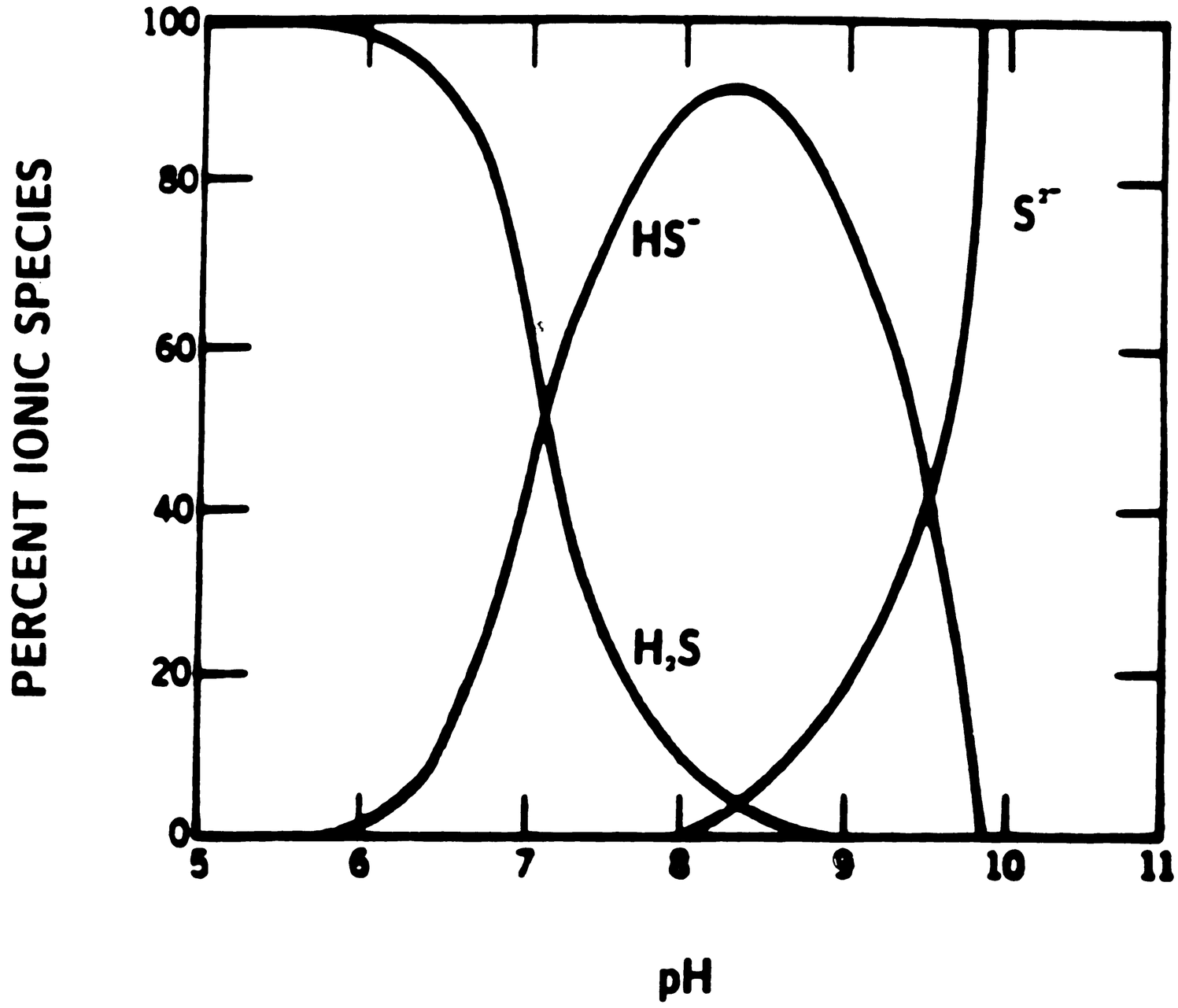


Figure 1-3: Predominance Diagram For Sulfide

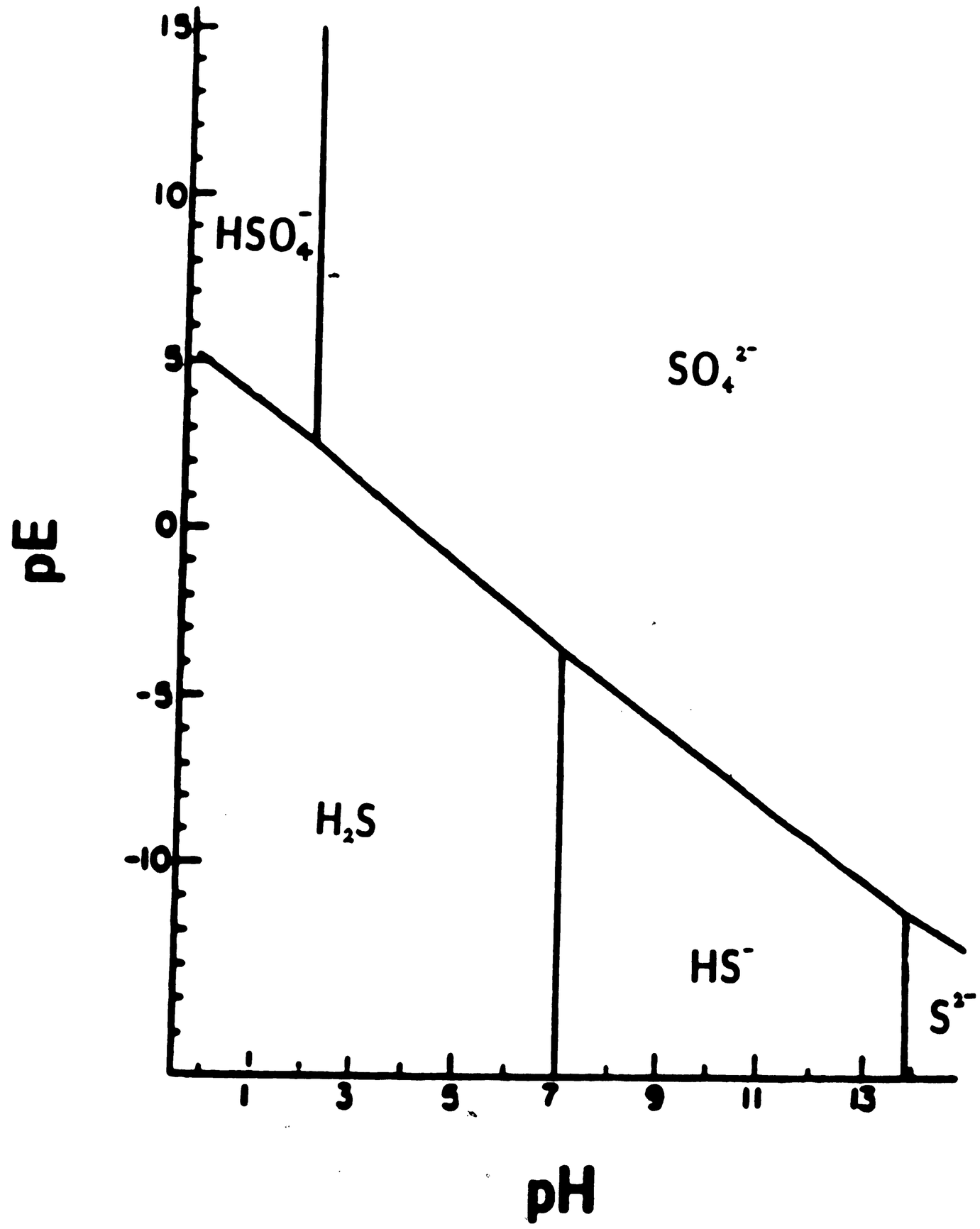


Figure 1-4: pE-pH Diagram For The Sulfate-Sulfide System

1.4 REMOVAL PROCESSES AND SHORTCOMINGS

Common treatment methods for the removal of arsenic, include lime or sulfide precipitation or coprecipitation with iron or aluminium hydroxide and adsorption onto coagulant floc with enmeshment of particulate arsenic. Other processes include adsorption onto activated carbon or alumina and ion exchange [4]. About 90 per cent removal of arsenic(V), at pH 7 or below, can be attained with conventional coagulation using iron and alum salts, for an initial arsenic(V) concentration of 0.1 mg/L[11]. Above pH 7, iron coagulation still results in high arsenic removal but alum coagulation removals drop with increasing pH. Lime softening is also very effective at pH values above 10.6 with removals as high as 100 per cent. Arsenic(III) removals similar to those of arsenic(V) can be achieved by conventional coagulation and lime softening, if the arsenic(III) is oxidised to arsenic(V) prior to treatment. Coagulation techniques would generate a sludge which would be contaminated with arsenic and might be considered hazardous. Disposal and dewatering of the generated hazardous sludge would also be a problem. High doses of coagulant would also increase the total dissolved solids content of the water being treated.

Ion exchange treatment using anion exchange resins or sorption, with activated alumina, or bone char can remove both forms of arsenic[2]. Arsenic is retained better than fluoride on activated alumina. Maximum equilibrium capacities for arsenic(V), on alumina, were achieved at a pH less than 7[11]. However, significant losses of alumina can occur over cycles of regeneration due to its amphoteric nature. Please note that regeneration of alumina is carried out using sodium hydroxide.

Selenium is associated primarily with wastewaters from coal mining, processing and combustion, plus wastewaters from sulfide ore milling and refining of metals. Petroleum-refining effluents are also reported to contain

selenium. Depending upon the industrial source, selenium occurs in the particulate or soluble form. Physical treatment processes such as sedimentation and filtration are quite effective when it occurs in the particulate form[4]. Soluble selenium removal is accomplished by conventional coagulation, activated alumina adsorption, ion-exchange and reverse osmosis. Lime precipitation of soluble selenium has been shown to be ineffective[4]. Coagulation using ferric sulfate removes only about 30 per cent or less of selenium(IV), for an initial selenium(IV) concentration of 0.1 mg/L, in the pH range of 6 to 7. Alum coagulation is more effective with upto 85 per cent removal at pH 5.5. A coagulant dose of about 100 mg/L(as ferric sulfate or alum) was required to achieve the stated removals using ferric and alum coagulation. The removals also decrease with increasing pH. Thus the selenium(IV) removal efficiency obtained using coagulation is low. Also, the removal efficiency is highly pH dependent.

Selenium(IV) is less preferred on strong base resins than nitrate but more preferred than chloride or bicarbonate. Hence, selenium(IV) removals would depend on the sulfate and nitrate concentrations in the water supply. The only effective treatment for soluble selenium appears to be anion exchange with preoxidation of selenite to selenate to enhance the anion exchange capacity[4].

Sulfide is normally removed by aeration or oxidation by chlorine. Waters treated for sulfide removal followed by filtration still exhibit a sulfurous odor. Presence of these odors could be due to the formation of polysulfides. However, studies have shown that polysulfide formation does not occur above pH 9[11]. Polysulfide formation is a shortcoming of this method of sulfide removal.

The shortcomings of the various removal techniques employed for the removal of arsenic, selenium and sulfide have been outlined in this section. Thus the need for an effective separation technique for the removal of trace

concentrations of these species exists.

1.5 NEED FOR SELECTIVE SORBENTS

Trace concentrations of contaminants can make water unfit for consumption or discharge into receiving bodies. Therefore, the goal of many water and wastewater treatment processes is the removal of certain target contaminants in the presence of other dissolved substances. A removal process that is often used is adsorption. This is a heterogeneous process where solid adsorbents preferentially pick up or adsorb dissolved contaminants. The viability of the adsorbent depends on the nature of the interaction between the target contaminant to be removed and the solid adsorbent used. For instance, activated carbon is an excellent adsorbent for high molecular weight and hydrophobic dissolved organic substances but is not very effective for the removal of inorganic ions such as arsenate, chromate, selenate, cadmium etc. The ability of activated alumina to remove anions drops sharply as the pH rises due to increased competition from hydroxyl ions. Also because of its amphoteric nature, significant loss of alumina occurs through dissolution after every cycle of operation, when regeneration is carried out with 2-8% sodium hydroxide.

Synthetic anion exchange resins could be used as sorbents in fixed bed processes due to their high exchange capacities(in the order of 1.0 meq/L)[14]. However, removal of toxic anions such as arsenate, arsenite, selenate and selenite from contaminated water (treated wastewater, surface water and groundwater) by anion exchange processes would be viable if the anion exchange resins are:

a) Selective toward the contaminant anions in the presence of other anions such as sulfate and chloride.

b) Can be regenerated efficiently so that the resin can be used over a

number of cycles.

A method for the treatment of selenite[4], using anion exchange, is its oxidation to selenate and the subsequent removal of selenate by anion exchange. This is because selenate is preferred over selenite by anion exchange resins. However, anion exchange selectivity for sulfate and selenate are nearly identical. Thus, ion exchange treatment of a selenate wastewater also containing appreciable levels of sulfate could result in low and uneconomical anion exchange capacity for selenium(VI) or selenate[4]. A column test was conducted with IRA-900, a typical strong base anion exchanger. Figure 1-5 is the effluent history for the test. The low affinity for selenite can be readily observed. Breakthrough of selenium(IV) occurred at about 50 bed volumes throughput, earlier than sulfate. Also, sulfate and selenate breakthrough occurred at the almost the same time. Thus, removal of selenium(IV) oxy-anions using a conventional anion exchange resin is not effective.

Calmon[15] reported the use of anion exchange for arsenic removal. The test samples contained 68 mg/L of arsenic(V) or arsenate. Batch type equilibrium tests with several different anion exchange resins in the chloride form showed removals of 55 to 82 percent. The latter removals were achieved using Ionac-260 weak base resin. The effect of variables such as pH and the presence of competing anions was not considered. Shen[5] conducted several experiments with the same weak base resin used by Calmon and obtained only 20.7 percent removal. He used synthetic water containing arsenic(III) or arsenite. Tests with "natural water" containing containing 0.84 mg/L of naturally occurring arsenic resulted in 100 percent removal. The difference in results could not be explained by him.

Ion exchange was used for arsenic removal by Welmoth, R.C. et. al at the USEPA Industrial Environmental Research Laboratory at Cincinnati Ohio. A

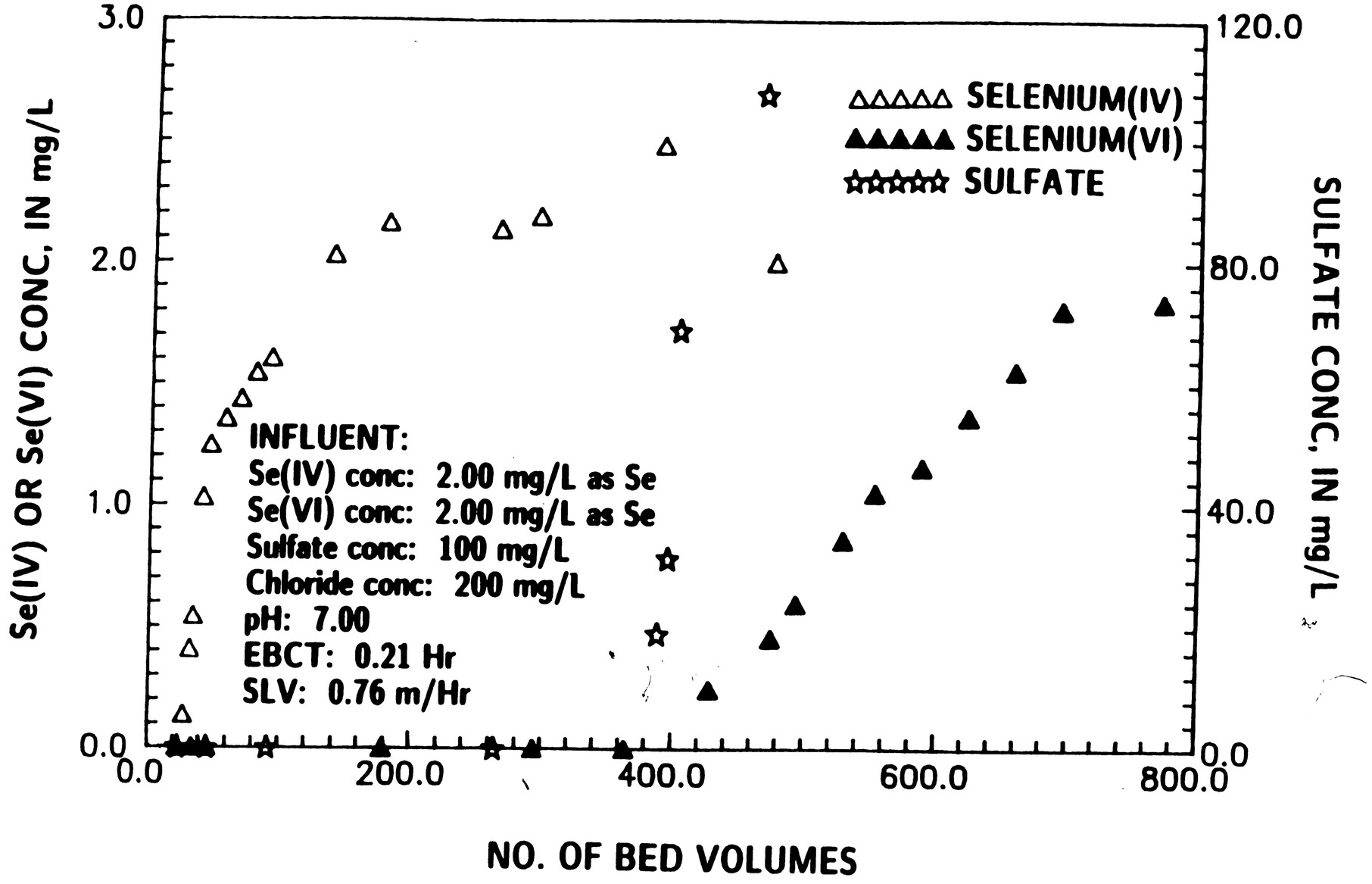


Figure 1-5: Effluent History For Column Run Using IRA 900

77 percent removal starting from an initial arsenic level of 2.3 mg/L was reported. Cumulative removals of 99.9 percent were reported for selenium using lime precipitation followed by anion exchange.

The selectivity sequence from the most preferred to the least preferred anion for a strong base anion exchanger is as follows[16]:

$Se(VI) > SO_4^{2-} > As(V) > NO_3^- > Se(IV) > Cl^-$

Thus sulfate ions have a higher affinity than arsenic(V) and selenium(IV) species. Maneval, Klein et al[16] made several attempts to modify the compositions of ion exchangers in order to improve the selectivity of the selenium(IV) species but were unsuccessful.

A chromatogram was obtained using a Dionex 4000i series ion chromatograph. Please see Figure 1-6. This instrument uses an anion separator column(which has a strong base anion exchange resin) and conductivity detection to determine the concentration of the anionic species in the sample being analysed. The elution time indicates the order of selectivity of the species. The least preferred anion has the shortest retention time and appears first, whereas the most preferred anion has the longest retention time and is eluted last. It can be seen that the selenium(IV) oxyanion is less selective than sulfate and selenate. Since sulfate ions are present in contaminated water and wastewater, the need for a selective sorbent is readily recognised.

1.6 PREMISES OF THE STUDY

1. Selenium and arsenic contamination of groundwater is fairly common. With groundwater being a source of potable water, evaluation of treatment processes for the removal of arsenic and selenium will become necessary.

2. Use of fixed bed processes for the selective removal of trace concentrations of arsenate and selenite, in the presence of other competing

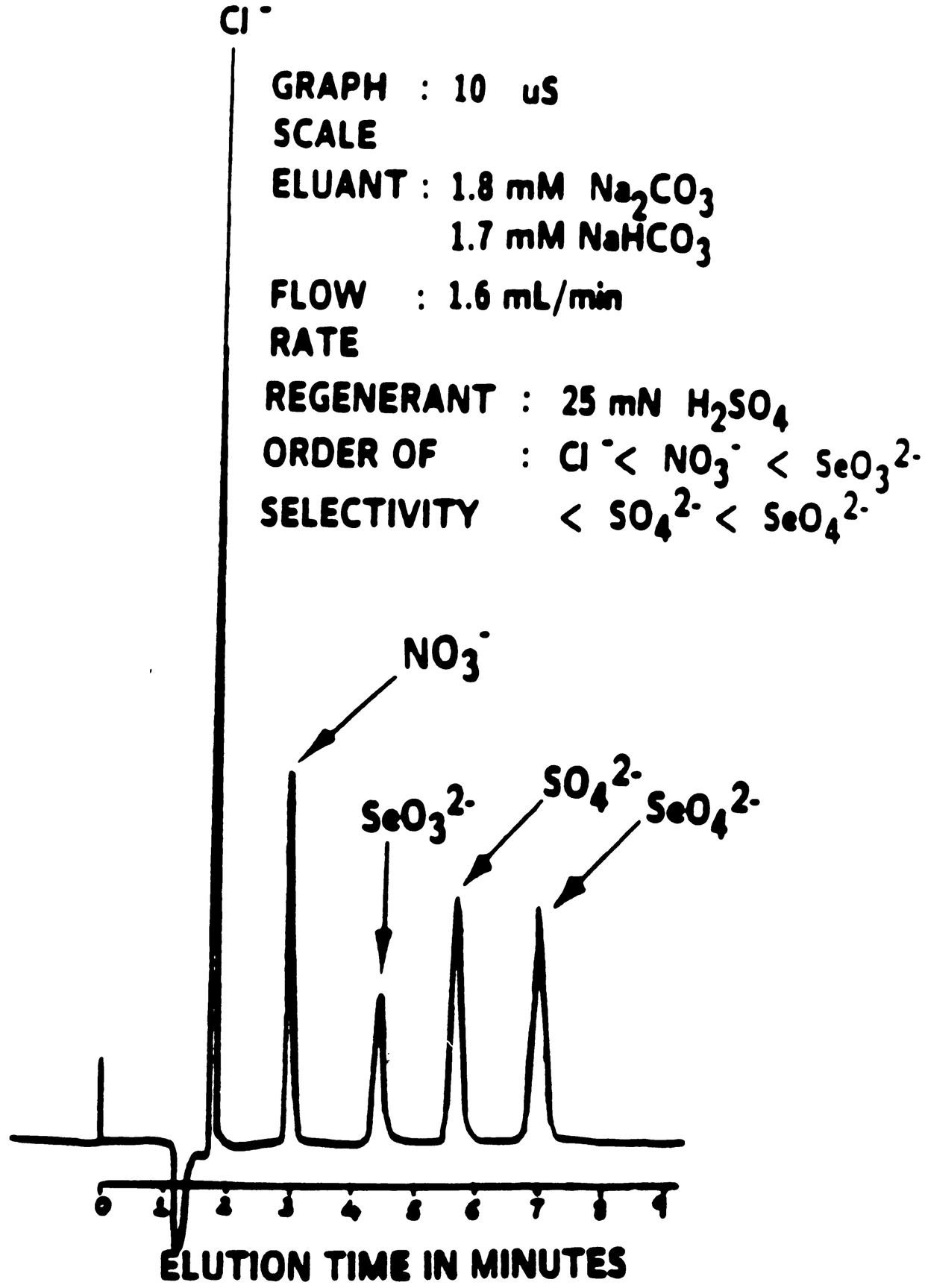


Figure 1-6: Ion Chromatogram Showing the Order of Selectivity of Various Anionic Species

solutes, requires sorbents with increased affinity towards the target species. Commonly used sorbents such as activated alumina, activated carbon and synthetic strong base anion exchange resins are not effective in this respect.

3. Strong base anion exchange resins are not suitable for the removal of trace quantities of selenium(IV) - commonly found in groundwater. This is because selenium(IV) is less preferred than the major groundwater anion sulfate[17]. There is very little information on the removal of arsenate by ion exchange. Arsenic removal is usually carried out using activated alumina. Studies by various researchers have shown that arsenic(V) is less preferred than sulfate by strong base anion exchange resins.

4. This study aims at overcoming the shortcomings of strong base anion exchange resins, conventionally used in fixed bed processes. It addresses the removal of trace concentrations of arsenic and selenium in the presence of high sulfate and chloride concentrations. This would be the situation if arsenic and selenium contaminated groundwater were to be treated.

1.7 OBJECTIVES OF THE STUDY

The objective of this study was to identify a class of sorbents for the selective removal of contaminant ions, namely, arsenate and selenite, in the presence of high chloride and sulfate concentrations. Arsenic and selenium contamination of groundwaters is common and their removal from these water supplies is a challenging separation problem. Therefore, the need for an effective sorbent is well recognized.

The study had the following objectives:

1. Identifying a new class of sorbents with a high preference for arsenate and selenite ions.

2. Studying the effects of various process variables such as pH, ionic

strength and the presence of competing species(or ligands) on the efficiency of the removal process.

3. To identify a suitable regenerant, to enable use of the sorbents over a number of cycles, to make the process cost-effective.

4. To identify a mechanistic model to explain the experimental observations.

Chapter 2
PROCESS APPROACH

2.1 LIGAND EXCHANGE INDUCED SORPTION: THE UNDERLYING CONCEPT

The need for a selective sorbent to remove arsenate, selenite and sulfide was realized in the previous chapter. An effective sorbent would have a high affinity for the target species, namely, arsenate, selenite and sulfide even in the presence of sulfate and chloride. The sorbent should also be amenable to efficient regeneration, to enable its repeated use over many cycles, to make it cost effective. A common feature of arsenate, selenite and sulfide is the low solubility of their copper compounds. Their formation constants[18] are listed in Table 2-1. Solubility products are written with reference to dissociation reactions. If the association of these ions with the copper ion is considered, the equilibrium constant may be written as the reciprocal of the solubility product. The equilibrium constant for the association reaction is otherwise called the formation or stability constant.

If the high formation constants of copper arsenate, copper selenite and copper sulfide could be utilized, selective removal of these anions by ligand exchange could be realised. This would be possible if the copper ion can be held onto a solid phase without losing its charges, thus enabling Lewis acid-base interaction between the copper ion and the anionic species.

A schematic representation of the process approach is indicated in Figure 2-1. Chelating ion exchangers would be the ideal synthetic sorbents to hold copper ions because of their high metal ion selectivity even under acidic conditions.

The sorbent chosen had the following characteristics:

Table 2-1: Formation Constants for Relevant Copper Compounds.

COMPOUND	SOLUBILITY PRODUCT	FORMATION CONSTANT * (STABILITY CONSTANT)
$CuCO_3$	$1.4x10^{-10}$	$7.1X10^{9}$
$Cu(OH)_2$	$2.2x10^{-20}$	$4.6X10^{19}$
CuS	$6.3x10^{-36}$	$1.6X10^{35}$
$CuSeO_3$	$2.1x10^{-8}$	$4.8X10^{7}$
$Cu_3(AsO_4)_2$	$7.6x10^{-36}$	$1.3X10^{35}$

* THE FORMATION CONSTANTS WERE OBTAINED BY INVERTING THE RESPECTIVE SOLUBILITY PRODUCTS

1. High affinity for the copper ion.

2. Anion exchange capacity.

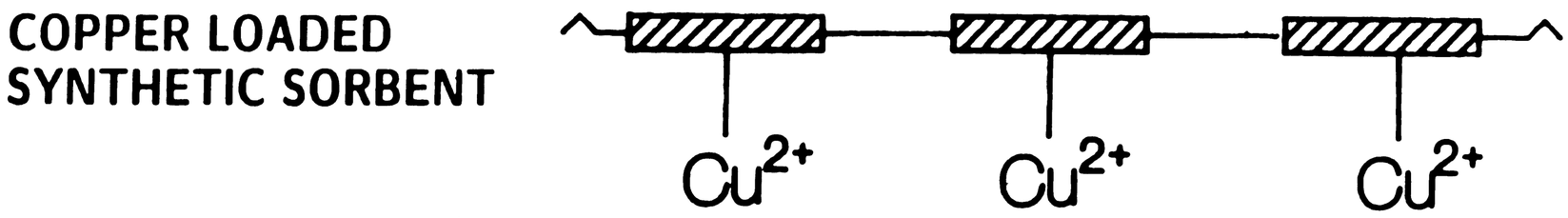
3. Operability over a wide range of pH.

4. Chemical and structural stability.

2.2 CHELATING ION EXCHANGERS WITH NITROGEN DONOR ATOMS

Chelating ion exchange resins are characterized by the presence of functionalities that are very selective toward metal ions. They have covalently bound side chains which contain one or more donor atoms. This high selectivity could be attributed to Lewis acid-base interaction. The donor atoms function as Lewis bases and can form coordinate covalent bonds with heavy metal ions which function as Lewis acids. Two chelating ion exchange resins, with nitrogen donor atoms were used in this study, namely, XFS 43084 and XFS 4195.

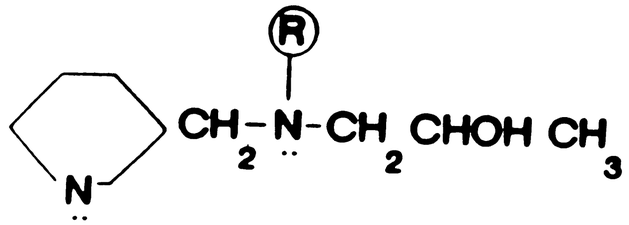
Chemical composition of the functional groups of the two resins are indicated in Figure 2-2. XFS 43084 has a pyridine functionality and a secondary amine group. For the sake of convenience, it will be referred to as DOW 2N(due to the presence of two nitrogen atoms). XFS 4195, has two pyridine molecules and a tertiary amine group. It will be referred to as DOW 3N (due to the presence of three nitrogen atoms). Of the two resins, DOW 3N has stronger chelating ability, due to the presence of three nitrogen atoms. Studies have shown that there is a one to one correspondence between the copper absorption and amine content of DOW 3N. This indicates that copper is absorbed as a 1:1 chelate[19]. Thus a higher uptake of copper can be expected since the number of nitrogen atoms is higher, thereby, favoring increased Lewis acid-base interaction.



HIGH AFFINTY SPECIES ⟶ SeO_3^{2-}, AsO_4^{3-}, S^{2-}

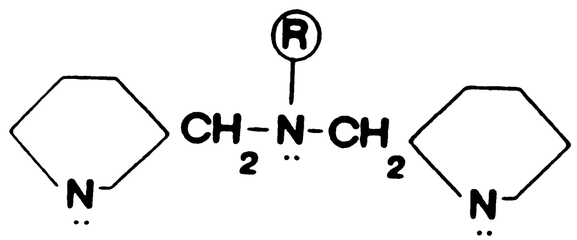
LOW AFFINITY SPECIES ⟶ SO_4^{2-}, Cl^-, NO_3^-

Figure 2-1: Process Approach



(2 N-Donor Atoms per Functional Group)

DOW 43084
(DOW 2N)



(3 N-Donor Atoms per Functional Group)

DOW 4195
(DOW 3N)

Figure 2-2: Chelating Functionalities with Multiple Nitrogen Donor Atoms

Figure 2-3 illustrates experimentally determined Me(II)/Ca separation factors, at pH 4.0, for the chelating exchangers- DP-1, IRC 718 and DOW 3N[20].

It can be readily seen that DOW 3N has a high affinity for the copper ion (separation factor is greater than 5000). From this figure it can be inferred that resins with nitrogen donor atoms show a high affinity for the copper ion. In fact, DOW 2N and DOW 3N, were synthesised and commercially introduced for hydrometallurgical applications in order to selectively remove Cu(II) at very acidic pH values in the presence of a high concentration of iron[21]. Therefore, these resins would be suitable to bind the copper ion onto a solid phase.

2.3 LIGAND EXCHANGE INDUCED SORPTION: A THERMODYNAMIC PERSPECTIVE

By binding the copper ion onto a solid phase(using a chelating polymer), selective removal of arsenate, selenite and sulfide could be achieved. The mechanism of uptake of these ions by copper loaded chelating resins could be viewed as a combination of ion exchange and Lewis acid-base interaction.

ΔG^0, the overall free energy change for the reaction can be given as the sum of two components,

$$\Delta G = \Delta G^o_{IX} + \Delta G^o_{LAB} \qquad 2.3.1$$

The above reaction can be rewritten as,

$$-RT\ln K_{overall} = -RT\ln K_{IX} - RT\ln K_{LAB} \qquad 2.3.2$$

or

$$K_{Overall} = K_{IX}\, K_{LAB} \qquad 2.3.3$$

Therefore, the overall equilibrium constant could be expressed as the product of two terms, K_{IX} and K_{LAB}. Where, K_{IX} refers to the interaction which is purely electrostatic and K_{LAB} refers to the interaction which is primarily Lewis acid-base in character[22].

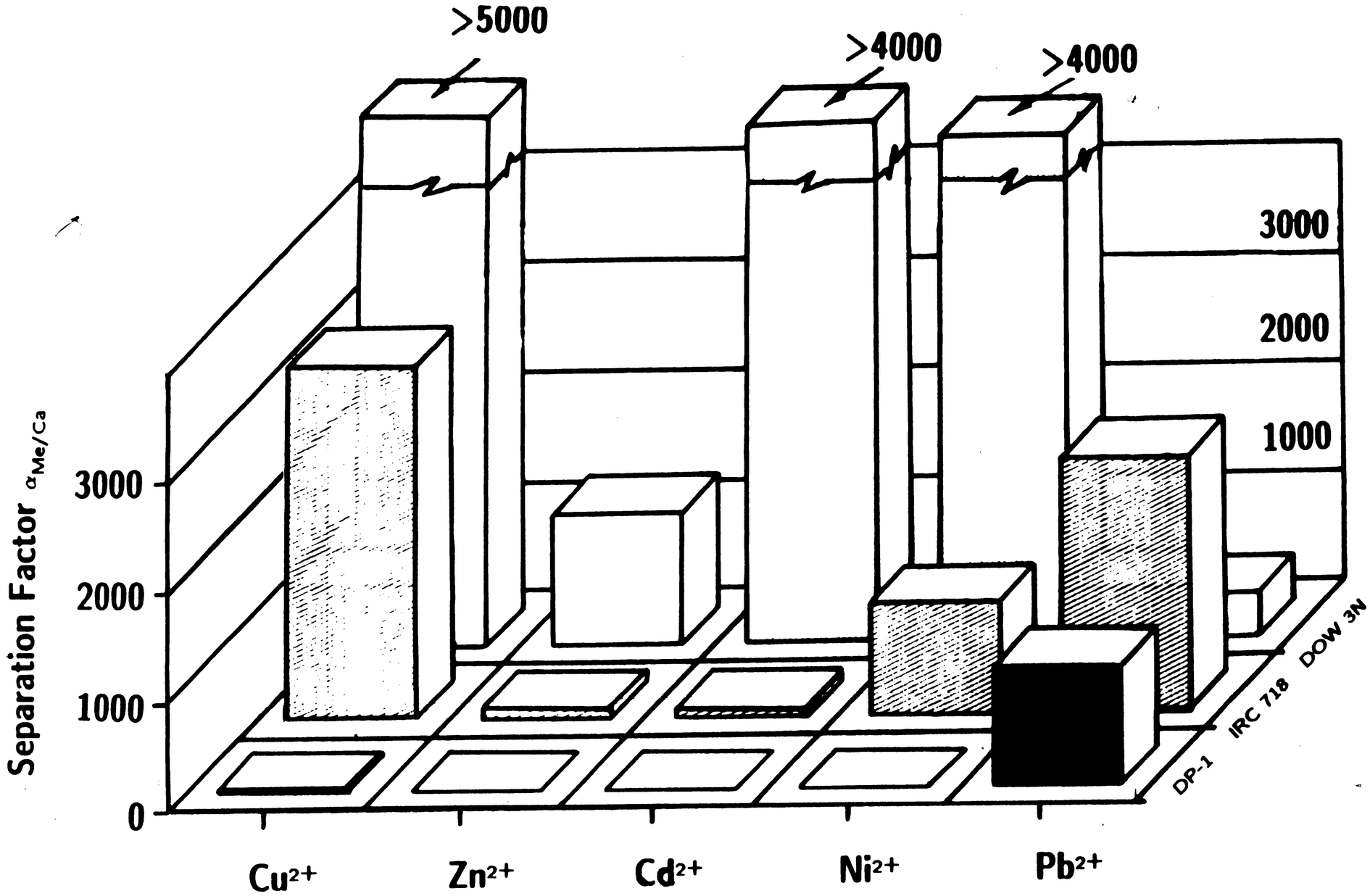


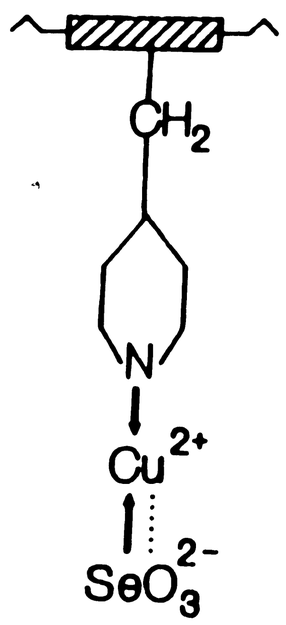
Figure 2-3: Metal/Calcium Ion Separation Factors For DP-1, IRC-718 and DOW 3N.

Conventional anion exchange involves uptake of anions through electrostatic interaction. The equilibrium constant for a such a reaction or exchange is given by K_{IX}. Therefore, the overall equilibrium constant will be represented by K_{IX} alone. The equilibrium constant for an interchange, which involves both electrostatic as well as Lewis acid-base interaction is therefore much higher. The corresponding free energy change at equilibrium is therefore more negative. This means that the reaction or interchange is more spontaneous and the corresponding uptake of species should therefore be much higher.

K_{LAB} is related to the formation constants of copper arsenate, copper selenite and copper sulfide. The formation constants for the various copper compounds of the species are indicated in Table 2-1. Figure 2-4 illustrates the mechanism by which anions are picked up by copper loaded DOW 2N. Please note that the selenite ion was chosen for the purpose of illustration. The figure also indicates the mechanism by which a conventional strong base anion exchanger(here, IRA 900) interchanges anions. Electrostatic interaction is the force holding the anions onto the resin.

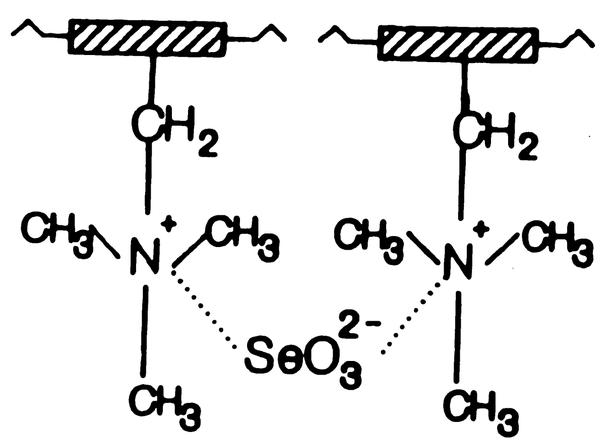
At this point it should be mentioned that the formation constants of the ferric compounds of arsenate, selenite and sulfide are also very high. Therefore, the Lewis acid-base interaction between the ferric ion and arsenate, selenite and sulfide respectively, should be very high. However, repeated efforts to load DOW 2N and DOW 3N with the ferric ion proved unsuccessful. Therefore, sorption of these ions by ferric loaded resins could not be investigated.

DOW 2N-Cu



Ion-Pair Formation
Due To Electrostatic and
Lewis Acid-Base Interaction

IRA 900



Ion-Pair Formation
Due To Electrostatic
Interaction

..... Ion-Pair Formation

——→ Lewis Acid-Base Interaction

Figure 2-4: Mechanism of anion uptake by a chelating exchanger versus an anion exchanger.

Chapter 3
EXPERIMENTAL PROCEDURES, MATERIALS AND EQUIPMENT

3.1 MATERIALS: ION EXCHANGE RESINS AND REAGENTS

The chelating polymers, DOW 2N and DOW 3N, used in this study were obtained from the DOW Chemical Co., MI. The strong base anion exchanger, IRA 900, with a quaternary ammonium functionality, and the weak acid chelating exchanger, IRC 718, were obtained from Rohm and Haas Co., Philadelphia. Table 3-1 gives some salient features of the resins used in this study. IRA 900 and IRC 718 were used for the sake of comparison. All the resins were obtained in spherical bead form with particle sizes varying from 0.3-0.8 mm.

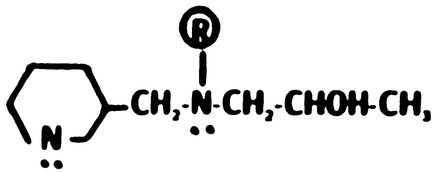
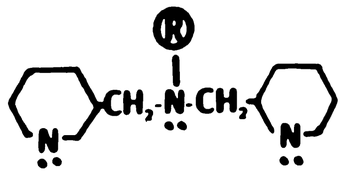
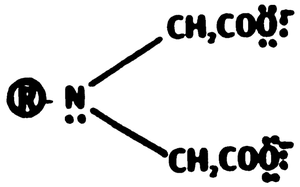
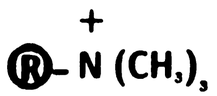
Sodium arsenate and sodium selenite were obtained from the Sigma Chemical Co. Sodium sulfide was obtained from the Fisher Chemical Co. All other chemicals were of analytical grade. Water used in sorption, titration and all other experiments was distilled and deionised, using a Barnstead ion exchange column.

3.2 PREPARATION OF SORBENTS

The resins were conditioned, by cyclic exhaustion, with 2% hydrochloric acid and 2% sodium hydroxide. After conditioning, the resins were washed with distilled deionised water.

DOW 2N, DOW 3N and IRC 718 were subsequently loaded with copper(II). 500 ppm $CuSO_4.5H_2O$ and/or $CuCl_2.2H_2O$ was used for this purpose depending upon the competing ion present - either sulfate or chloride. The resin used for the column run was converted into the copper form using $CuCl_2.2H_2O$.

Table 3-1: Salient Features Of Ion Exchangers Used In This Study

Functionality	Donor Atoms Per Functional Group	Matrix	Acid/Base Characteristic	Manufacturer and Trade Name
	2 "N" Atoms	Polystyrene	Weak Base	Dow Chemical, Dow 2N or XFS 43084
	3 "N" Atoms	Polystyrene	Weak Base	Dow Chemical, Dow 3N or XFS 4195
	1 "N" Atom and 2 "O" Atoms.	Polystyrene	Weak Base and Weak Acid	Rohm and Haas, IRC 718
	None	Polystyrene	Strong Base	Rohm and Haas, IRA 900

The solutions of cupric sulfate and cupric chloride were at pH 5.0. The copper loaded resins were then washed with distilled deionised water and air dried. The copper capacity of DOW 2N was estimated to be 1.67 meq/gm dry resin and the copper capacity of DOW 3N was estimated to be 2.453 meq/gm dry resin. IRA 900 was converted into the chloride form for the respective column run. This was done using 2% brine. The resin was washed with distilled deionised water to remove excess brine.

3.3 SORPTION EXPERIMENTS

Experiments were conducted to study the sorption equilibria between the ion-exchange resins and aqueous solutions of anions: arsenate, selenite and sulfide. The chelating polymers, DOW 2N and DOW 3N, have weak base functionalities. Thus they have a high affinity for the hydrogen ion. A constant pH would therefore be difficult to maintain in batch equilibration tests. Batch equilibration involves agitation of a weighed amount of the resin with a definite volume of solution containing a known concentration, of the species whose uptake is being studied. The agitation is carried out until the concentration of the species in the supernatant solution is constant.

The equilibrium data, for arsenate and selenite, in this study were generated using short columns of inner diameter 1.0 cm. The influent to each column was of a fixed composition i.e., with a known concentration of arsenate or selenite in the presence of a constant competing ion(sulfate or chloride) concentration at a fixed pH. About 0.2 gm of resin was placed in each short glass column. Five columns were used to generate five data points for each isotherm. The temperature during all the tests was the ambient room temperature of $25°C + 2°C$. The volume of solution fed was in excess of the stoichiometric requirement to ensure that equilibrium was attained. This was

also checked by comparing the effluent and the influent concentration of the species being studied. The experiment was stopped when both the influent and the effluent species concentration was the same for a period of more than three days. Following equilibration, the exhausted resin was washed by passing distilled deionised water through the columns. The resin, in each column, was then regenerated using a 2% ammonia solution. When uptake of arsenic(V) and selenium(IV) was studied using IRC 718, 2% hydrochloric acid was used to regenerate the resin. The regenerant was analysed for copper and the species under consideration- arsenic(V) or selenium(IV). The uptake, by the resin, at equilibrium was computed by mass balance calculations.

The sulfide isotherms were determined by batch equilibration. The pH was checked and adjusted every 2 hrs. This method of equilibration was used because of the volatile nature of the sulfide species and lack of suitable apparatus to carry out the experiment using a column set-up. Controls were used to check for the loss of sulfide through volatilization. The sorption experiments were carried out by equilibrating 0.05-0.1 gm of resin with 200 ml of sulfide solutions, with known concentrations of sulfide, in 250 ml Nalgene bottles. A mechanical agitator was used for agitation. A concentration range of 10 to 100 ppm was used in order to be able to detect losses through volatilization by ensuring a high residual concentration of sulfide after equilibration. These experiments had to be conducted at a very alkaline pH - 9.5 to 10.5 to ensure that sulfide was present as HS^- or S^{2-} to a greater extent (pK_1 of H_2S= 7.1 and pK_2= 14.0). Competition due to the presence of hydroxyl ions was ruled out on the basis that the solubility product of $Cu(OH)_2$ ($K_{sp}=2.2\times10^{-20}$)is greater than the solubility product of CuS ($K_{sp}=6.3\times10^{-36}$). Therefore, the formation constant of CuS is higher than that of $Cu(OH)_2$. The procedure for regeneration mirrored the sorption procedure. After equilibration and analysis of the supernatant for

sulfide, the spent sorbent was washed with deionised water and placed in a 250 ml bottle with 200 ml of 10% ammonia. After agitation for 2 hrs, the supernatant was filtered and agitated with about 1.5 gms of DP-1(in calcium form) to remove copper. This was done to prevent the blue color of the cuprammine complex from interfering with the colors produced during the estimation of sulfide by iodometry.

Please see Appendix A for a brief description of sorption equilibria and sorption isotherms.

3.4 FIXED BED COLUMN RUNS

Three fixed bed column runs were performed using a column of internal diameter 1.0 cm. The resin bed depth was 12.6 cm. DOW 2N and DOW 3N were placed in the column and loaded with copper by pumping copper chloride solution downflow through the resin bed, before starting the respective column runs. The copper loaded resins were washed with distilled deionised water, before starting the column runs. A fractional horsepower(1/30 HP) gear motor pump was used for pumping solutions through the resin bed. The experimental set-up is shown in Figure 3-1. The samples were collected in 25 ml test tubes using an ISCO Cygnet fraction collector(2170-002 series). The sample collection time was 30min and a flow rate of 0.75 cc/min was employed for all the column runs. Elution of spent DOW 2N and DOW 3N was carried out using 2% ammonia. The eluate was collected at 10 min intervals and an eluant flow rate of 0.25 cc/min was employed for the purpose. Spent IRA 900 was regenerated using 2% brine. The same flow rate and collection time as the previous runs was used for the purpose of regeneration.

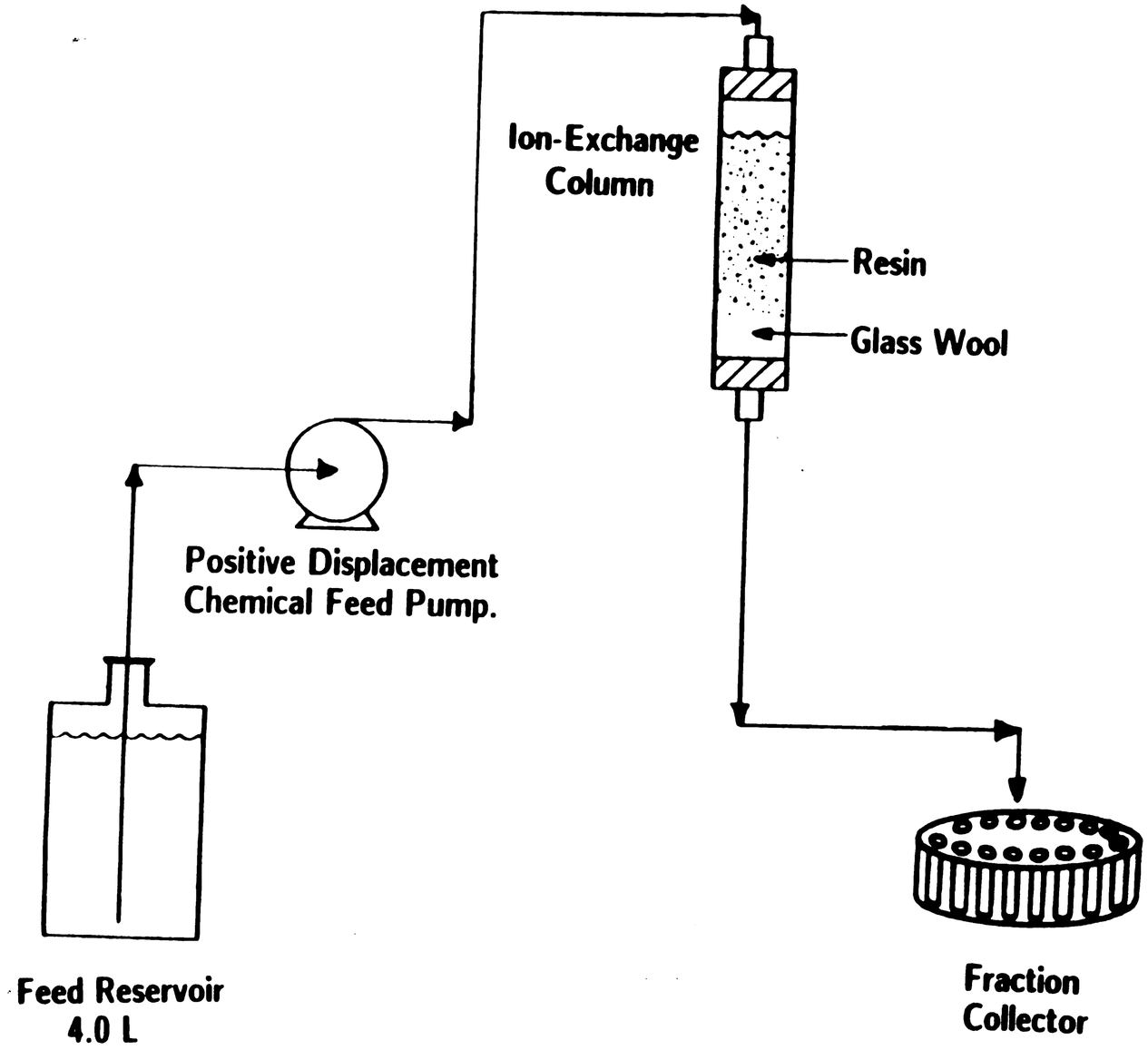


Figure 3-1: Experimental Set Up For Column Tests

3.5 ANALYSIS METHODS

An atomic absorption spectrophotometer(Perkin Elmer Model 2380) was used in the flame mode or with the graphite furnace attachment for analysis. Arsenic(V) and selenium(IV) were analysed using the graphite furnace atomic absorption technique. An electrodeless discharge lamp for selenium and arsenic was used as the light source. All sample injections were 20 uL followed by 20 uL of $NiNO_3$(1000 ppm as Ni). Sulfate, chloride and selenium(IV) were analysed using an ion chromatograph(Dionex Model 4500i series) by conductivity detection. The sulfide ion was analysed by iodometry[23]. Bicarbonate was analysed by titration[23]. A Total Organic Carbon Analyser (Beckmann Model 915B) was also used for the estimation of bicarbonate as total carbon.

pH measurements were made using a Fisher accumet model 930 pH meter. The electrode was calibrated to read in the acidic as well alkaline range. Suitably diluted sodium hydroxide was used for pH adjustment on the alkaline side. pH on the acidic side was adjusted using suitably diluted hydrochloric or sulfuric acid.

Chapter 4
EXPERIMENTAL RESULTS AND DISCUSSION

4.1 EQUILIBRIUM SORPTION STUDIES AND COLUMN RUNS

The effectiveness of copper loaded chelating exchangers(with pyridine functionalities) in removing arsenate, selenite and sulfide was tested by conducting specific laboratory experiments. The synthetic sorbents used were copper loaded DOW 2N and DOW 3N, hereafter, referred to as DOW 2N-Cu and DOW 3N-Cu.

Two types of experiments were conducted to determine the performance of the sorbents:

1. Equilibrium tests.

2. Dynamic column runs.

The following specific equilibrium tests were conducted:

1. Studies were conducted to determine the sorption isotherms for selenite and arsenate, in the presence of the competing ions, sulfate and chloride, for the various sorbents. The sorbents investigated were DOW 2N-Cu, DOW 3N-Cu, IRA 900 and copper loaded IRC 718.

2. The effect of pH on selenite uptake, by DOW 2N-Cu, was also studied. The sulfate and selenium concentrations were held constant during the experiment.

3. Selenite uptake in the presence of bicarbonate, as the competing ion, was studied, using DOW 2N-Cu as the sorbent. The effect of

pH, on arsenate and selenite uptake, in the presence of bicarbonate was also investigated.

4. Uptake of sulfide, by DOW 2N-Cu and DOW 3N-Cu, in the presence of a high sulfate concentration was also studied.

The following fixed-bed column runs were conducted:

1. A column run using DOW 2N-Cu as the sorbent.

2. A column run using IRA 900, to compare the performance of a conventional anion exchanger to that of DOW 2N-Cu.

3. A column run using DOW 3N-Cu as the sorbent.

4.1.1 STUDIES ON SELENITE AND ARSENATE REMOVAL

1. COMPARISON OF DOW 2N-Cu AND IRA 900 WITH RESPECT TO ANION UPTAKE

The structure of IRA 900, a strong base anion exchanger, with a quaternary ammonium functionality, and that of DOW 2N are indicated in Table 3-1. Figure 4-1 compares the arsenate uptake by DOW 2N-Cu and IRA 900. The experiment was conducted at pH 8.5 and a constant competing ion(in this case sulfate) concentration of 250 mg/L. The experimentally determined separation factors are tabulated in Table 4-1. The arsenic(V)-sulfate separation factor, for various aqueous phase concentrations of arsenic(V), was fairly constant and around 35. Such a high arsenate-sulfate separation factor has not been reported for any synthetic sorbent. Please note that arsenate is the oxy-anion of arsenic(V). All concentration measurements were made as total arsenic, in mg/L as As. The As(V)/SO_4^{2-} separation factor is defined as follows:

$$\alpha_{As/SO_4} = \frac{[\overline{As(V)}]\,[SO_4^{2-}]}{[As(V)]\,[\overline{SO_4^{2-}}]} \qquad 4.1.1$$

The quantities within square brackets are the aqueous phase concentrations of the respective species, in mg/L, and the quantities with an overbar represent the resin phase concentrations of the species in mg per gm of air-dry sorbent. Figure 4-2 compares the arsenate-sulfate separation factors determined for DOW 2N-Cu and IRA 900, under identical experimental conditions. The arsenate-sulfate separation factor for DOW 2N-Cu is about 150 times greater than that for IRA 900. Table 4-2 gives the values of the arsenate-sulfate separation factor computed for IRA 900[24].

Copper arsenate, as indicated in Table 2-1, is a copper compound with a high stability constant. This would mean that arsenate should have a high affinity for the resin-held copper ion. The high uptake, of arsenate by DOW 2N-Cu, can be attributed to the mechanism of ion exchange accompanied by Lewis acid-base interaction.

A column run was carried out using IRA 900 in the chloride form. Fig 4-3 gives the effluent history of the run. It can be seen that selenite breakthrough occurs much before sulfate or selenate(oxy-anion of selenium(VI)). Thus this exchanger would not be useful for removing trace concentrations of selenium(IV) in the presence of high concentrations of sulfate. The test results also validated the order of selectivity of anionic species as shown in the ion chromatogram, Figure(1-6). Please note that a strong base exchanger is also used in the ion chromatograph for conductivity detection of anions. In the column run, selenate breakthrough occurred after sulfate, as it is the most preferred species. Selenite is the least preferred species and its breakthrough occurred at about 25 bed

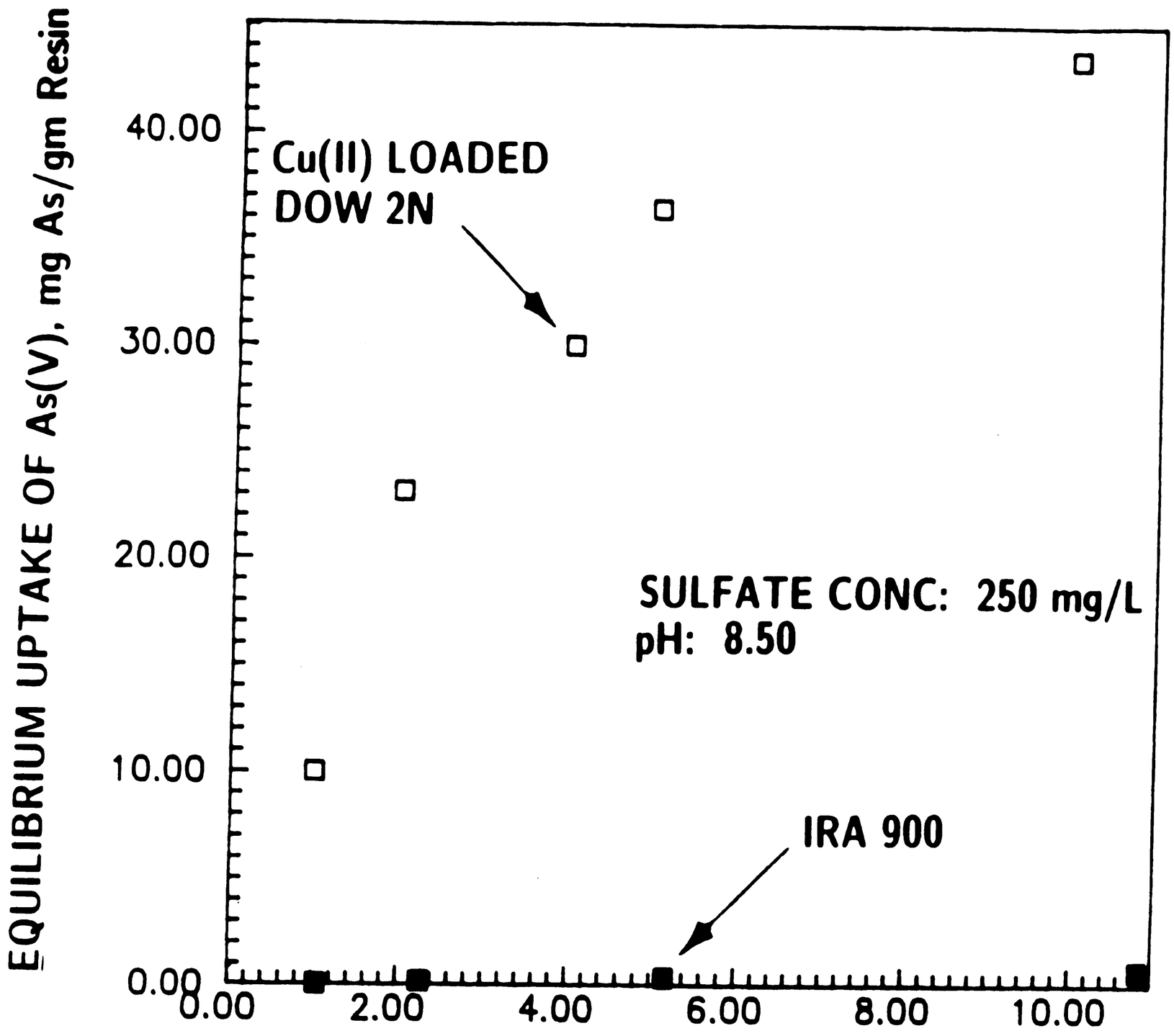


Figure 4-1: Comparison of Arsenate Uptake by DOW 2N-Cu And IRA 900

Serial No.	Aqueous Phase As(V) Conc, [As], in mg/L as As	Aqueous Phase Sulfate Conc, $[SO_4^{2-}]$, in mg/L	Resin Phase As(V) Conc, q_{As}, in mg/gm Resin	Resin Phase Sulfate Conc, q_{SO_4}, in mg/gm Resin	Separation Factor, $\alpha_{As/SO_4} = \frac{q_{As}\,[SO_4]}{[As]\,q_{SO_4}}$
1	1.00	250	9.97	75.35	33.10
2	3.35	250	23.13	47.12	36.63
3	4.00	250	29.96	51.84	36.12
4	5.00	250	36.37	44.67	40.71
5	10.00	250	43.55	33.73	32.28

Table 4-1: Arsenate-Sulfate Separation Factor For DOW 2N-Cu At pH 8.5

Serial No.	Aqueous Phase As(V) Conc, [As], in mg/L as As	Aqueous Phase Sulfate Conc, $[SO_4^{2-}]$, in mg/L	Resin Phase As(V) Conc, q_{As}, in mg/gm Resin	Resin Phase Sulfate Conc, q_{SO_4}, in mg/gm Resin	Separation Factor, $\alpha_{As/SO_4} = \frac{q_{As}\,[SO_4]}{[As]\,q_{SO_4}}$
1	1.00	250	9.97	75.35	33.10
2	3.35	250	23.13	47.12	36.63
3	4.00	250	29.96	51.84	36.12
4	5.00	250	36.37	44.67	40.71
5	10.00	250	43.55	33.73	32.28

Table 4-1: Arsenate-Sulfate Separation Factor For DOW 2N-Cu At pH 8.5

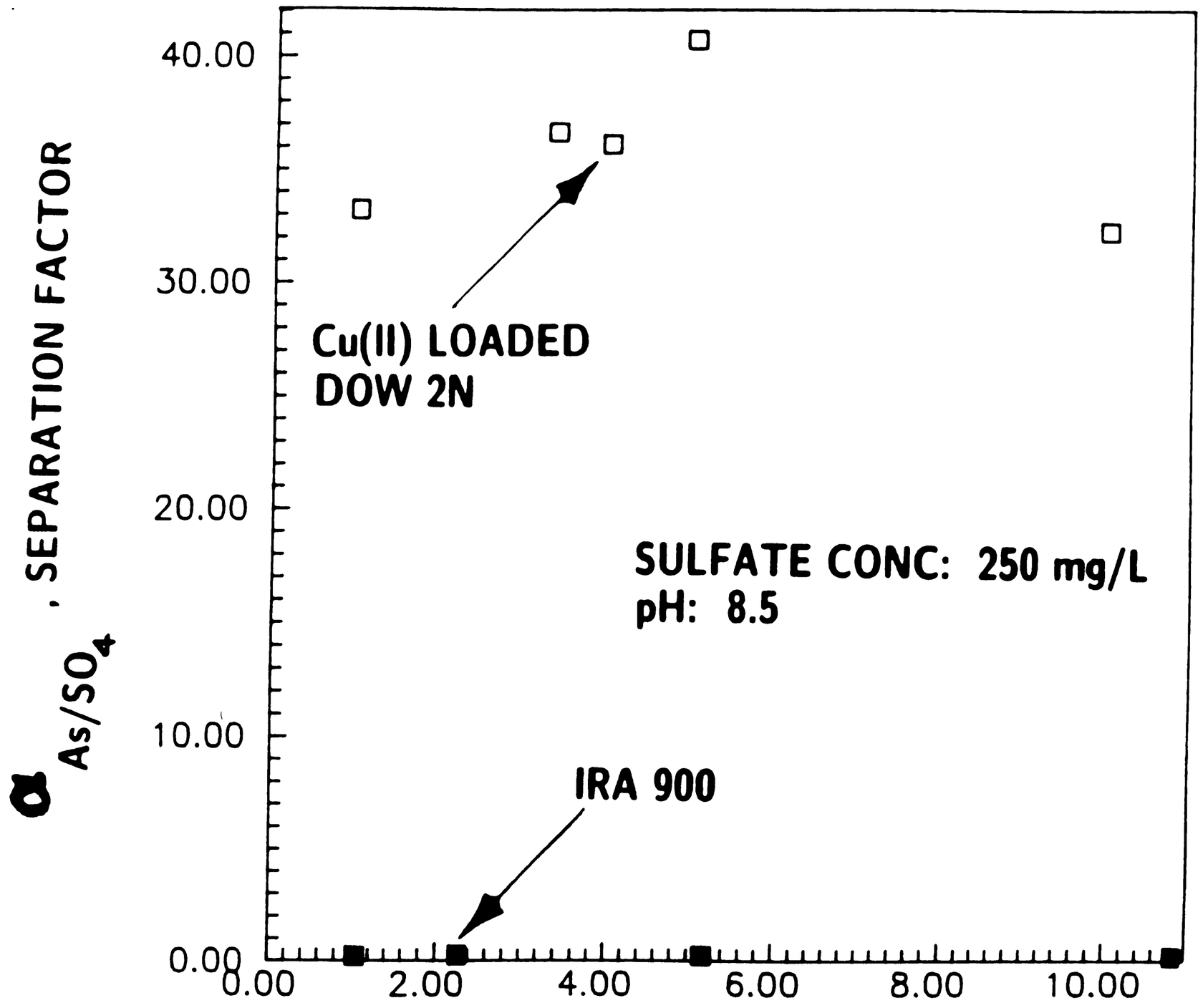


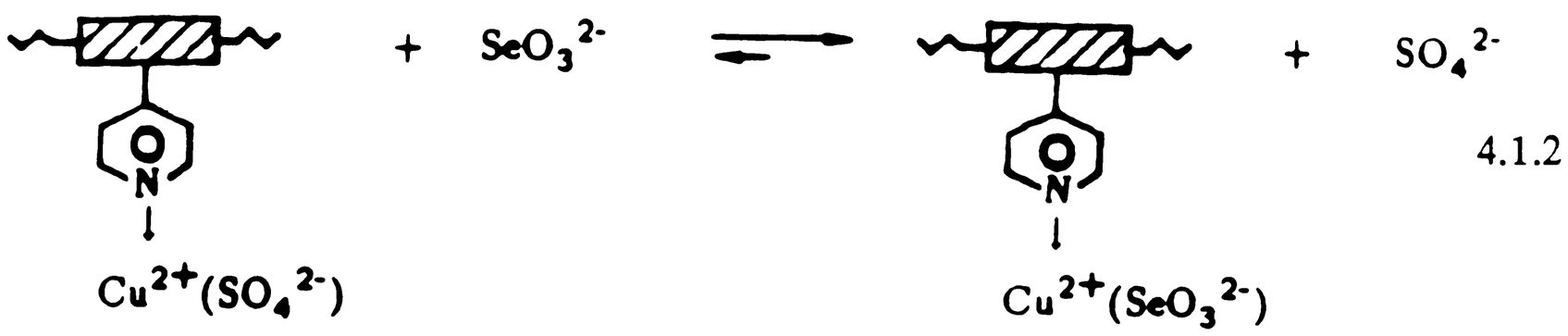
Figure 4-2: Comparison Of The Arsenate-Sulfate Separation Factor For DOW 2N-Cu And IRA 900

Serial No.	Aqueous Phase As(V) Conc, [As], in mg/L as As	Aqueous Phase Sulfate Conc, $[SO_4^{2-}]$, in mg/L	Resin Phase As(V) Conc, q_{As}, in mg/gm Resin	Resin Phase Sulfate Conc, q_{SO_4}, in mg/gm Resin	Separation Factor, $\alpha_{As/SO_4} = \frac{q_{As}\,[SO_4]}{[As]\,q_{SO_4}}$
1	1.04	250	0.17	206.21	0.208
2	2.28	250	0.49	205.59	0.264
3	5.18	250	1.05	204.76	0.246
4	10.86	250	1.90	203.32	0.206

Table 4-2: Arsenate-Sulfate Separation Factor For IRA 900 At pH 8.5

volumes throughput. As is evident from the effluent history plot, selenite underwent chromatographic elution because it is the least preferred species.

A column run was also conducted using DOW 2N-Cu as the sorbent. Figure 4-4 gives the effluent history of the run. Selenite breakthrough occurred much later than sulfate, close to 1000 bed volumes throughput. The pH of the influent was maintained at 9.5 to ensure that the major fraction of the total selenium(IV) was present as the divalent selenite ion, SeO_3^{2-}. The selenite-sulfate interchange, for this case, can be represented as follows:



4.1.2

This high selectivity of DOW 2N-Cu, for the selenite ion can be attributed to ion exchange accompanied by Lewis Acid-Base interaction. As shown in Table 2-1, copper selenite has a high formation constant, indicating a strong affinity of the resin-held copper ion for the aqueous phase selenite ion.

2. ADDITIONAL STUDIES USING DOW 2N-Cu AS THE SORBENT

The selenite-chloride isotherm for DOW 2N-Cu, at pH 7.00, is shown in Figure 4-5.

The competing chloride ion concentration is 250 mg/L. The computed

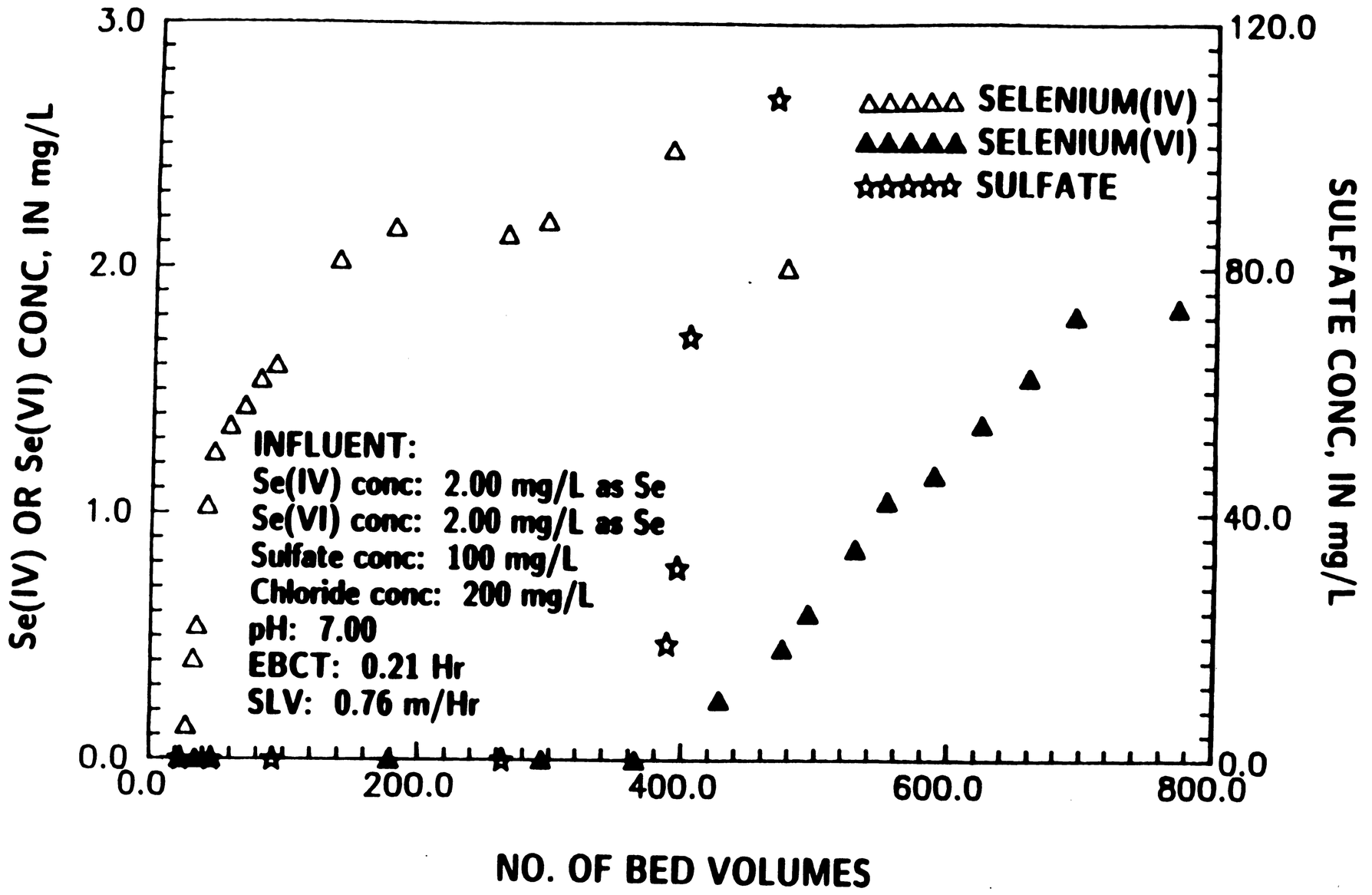


Figure 4-3: Effluent History Plot For The Column Test Using IRA 900 In The Chloride Form

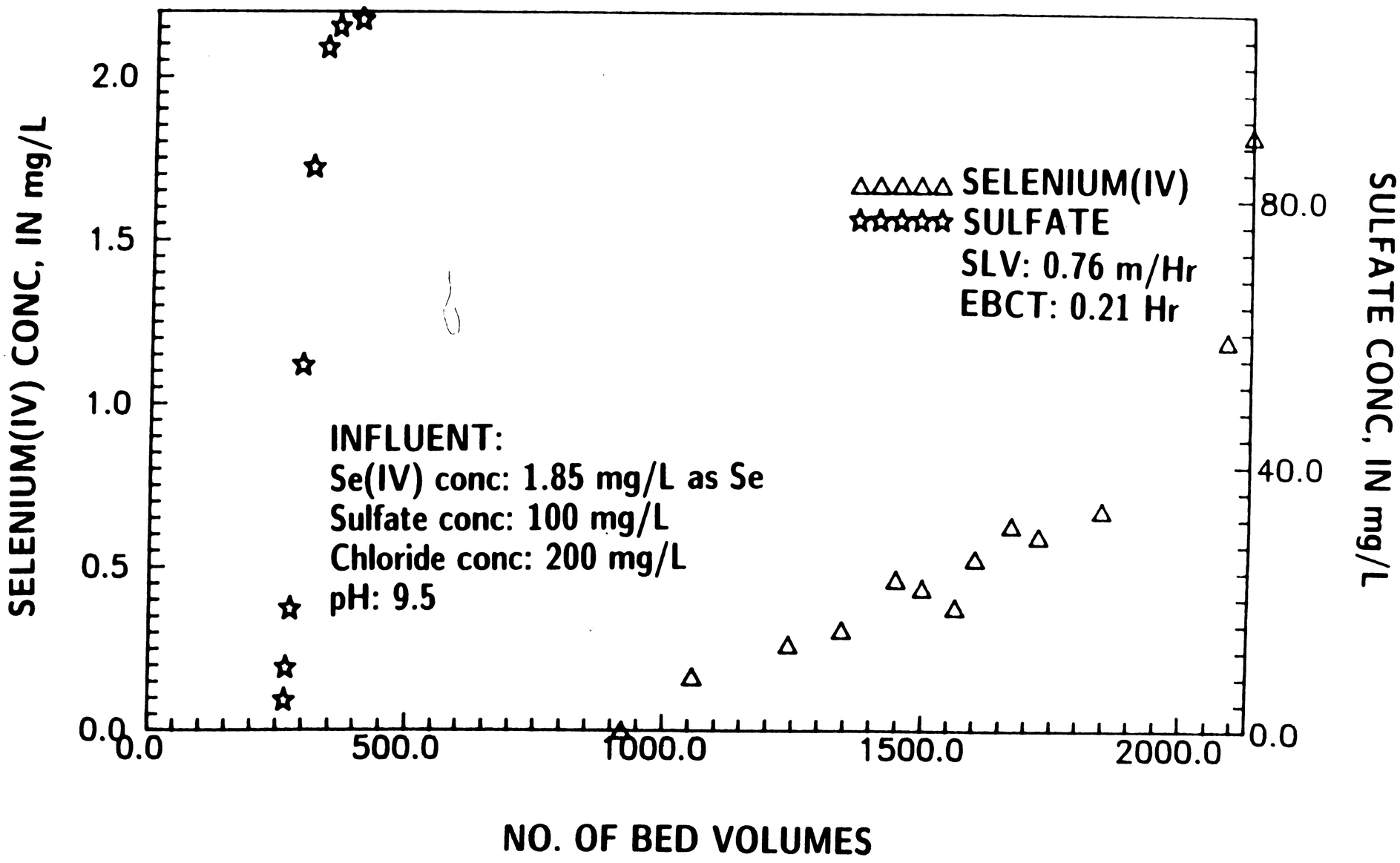


Figure 4-4: Effluent History Plot For The Column Test Using DOW 2N-Cu

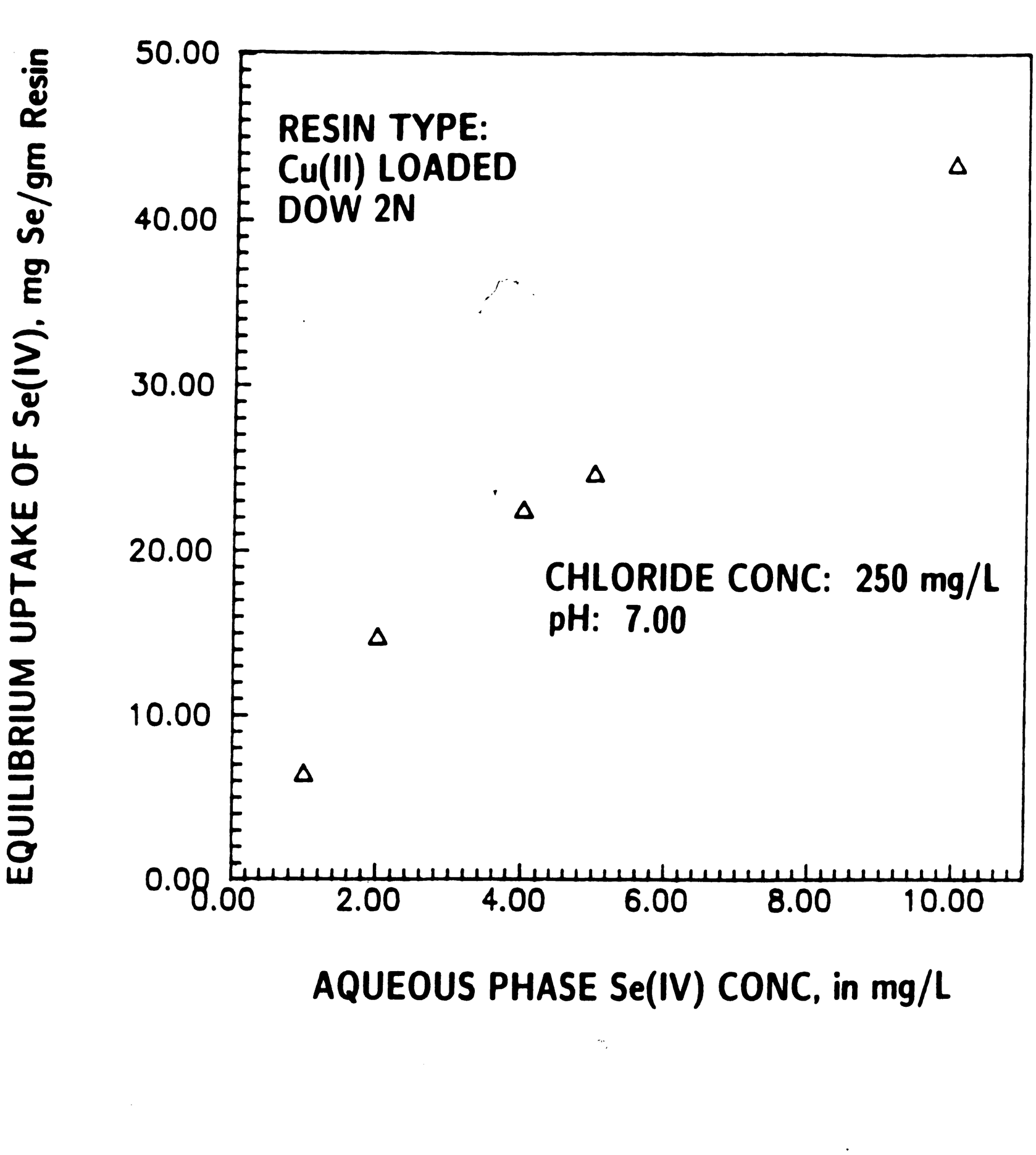


Figure 4-5: Selenite-Chloride Isotherm For Dow 2N-Cu At pH 7.00

separation factors are indicated in Table 4-3. The selenite-chloride separation factor is defined as:

$$\alpha_{Se/Cl} = \frac{[\overline{Se(IV)}]\,[Cl^-]}{[Se(IV)]\,[\overline{Cl^-}]} \qquad 4.1.3$$

It can be seen that selenite is the preferred species(separation factor is about 62). Thus, DOW 2N-Cu is a suitable sorbent for the selective removal of trace concentrations of selenite in the presence of a high concentration of chloride(the competing ion).

Figure 4-6 is the selenite-sulfate isotherm. The competing ion(sulfate) concentration was held constant at 250 mg/L and the experiment was conducted at pH 7.00. The separation factor, as indicated in Table 4-4, is around 10. The selenite-sulfate separation factor being defined as:

$$\alpha_{Se/SO_4} = \frac{[\overline{Se(IV)}]\,[SO_4^{2-}]}{[Se(IV)]\,[\overline{SO_4^{2-}}]} \qquad 4.1.4$$

Thus, by experiment it was proved that DOW 2N-Cu shows increased selectivity for the selenite ion in the presence of sulfate. This is in contrast to what was observed in the case of IRA 900.

3. EFFECT OF pH

Figure 4-7, shows the effect of pH on selenium(IV) uptake in the presence of sulfate, for DOW 2N-Cu. The separation factor was observed to increase with increasing pH. The selenium-sulfate separation factor, as determined at the various pH values, is indicated in Table 4-5. The experimental observation could be explained as follows. As pH increases, the fraction of $C_{T,Se}$ that is

Serial No.	Aqueous Phase Se(IV) Conc, [Se], in mg/L as Se	Aqueous Phase Chloride Conc, $[Cl^-]$, in mg/L	Resin Phase Se(IV) Conc, q_{Se}, in mg Se/gm Resin	Resin Phase Chloride Conc, q_{Cl}, in mg/gm Resin	Separation Factor, $\alpha_{Se/Cl} = \frac{q_{Se}\,[Cl]}{[Se]\,q_{Cl}}$
1	1.00	250	6.47	25.81	62.55
2	2.00	250	14.77	31.22	59.22
3	4.00	250	22.46	22.44	62.52
4	5.00	250	24.65	19.51	63.21
5	10.00	250	43.43	17.53	61.97

Table 4-3: Selenite-Chloride Separation Factor For DOW 2N-Cu At pH 7.00

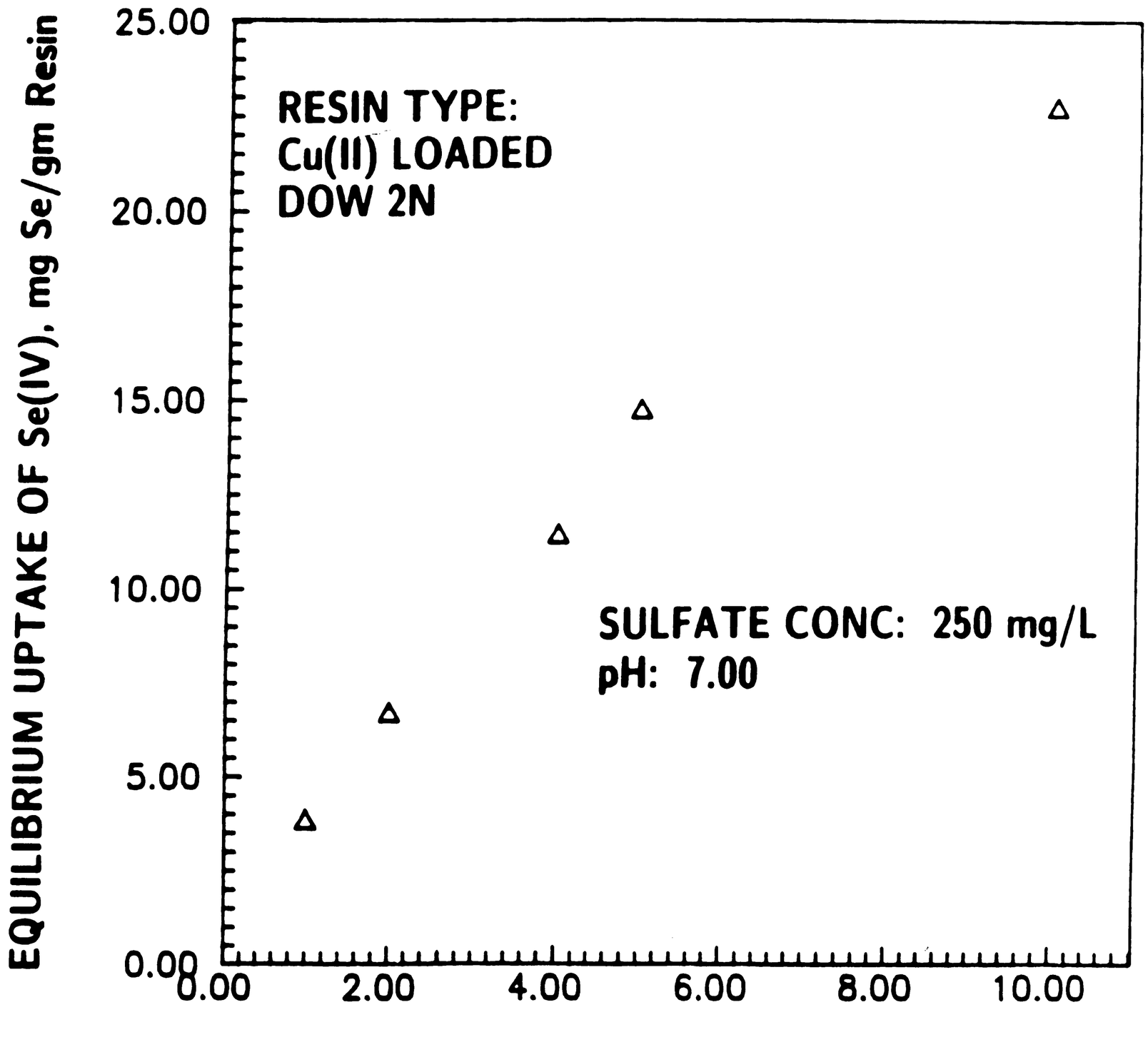


Figure 4-6: Selenite-Sulfate Isotherm For DOW 2N-Cu At pH 7.00

Serial No.	Aqueous Phase Se(IV) Conc, [Se], in mg/L as Se	Aqueous Phase Sulfate Conc, $[SO_4^{2-}]$, in mg/L	Resin Phase Se(IV) Conc, q_{Se}, in mg Se/gm Resin	Resin Phase Sulfate Conc, q_{SO_4}, in mg/gm Resin	Separation Factor, $\alpha_{Se/SO_4} = \frac{q_{Se}\,[SO_4]}{[Se]\,q_{SO_4}}$
1	1.00	250	3.84	89.11	10.77
2	2.00	250	6.72	79.21	10.62
3	4.00	250	11.47	74.26	9.65
4	5.00	250	14.77	69.30	10.66
5	10.00	250	22.75	59.40	9.58

Table 4-4: Selenite-Sulfate Separation Factor For DOW 2N-Cu At pH 7.00

present as SeO_3^{2-} increases. This is because pK_1 for selenious acid is 2.6 and the pK_2 is 7.9.

As pH increases the SeO_3^{2-} concentration increases and the forward reaction, as represented in equation 4.1.2, is favored by the law of mass action. Therefore, uptake of selenium(IV) increases and the separation factor increases. At low pH values, due to the speciation of the selenium(IV) oxyanion, the biselenite ion($HSeO_3^-$) is the predominant species. Interchange would be predominantly electrostatic, leading to low separation factors. At high pH values, due to the presence of the selenite ion, interchange would involve both electrostatic as well as Lewis Acid-Base interaction.

The resin phase concentration of selenium(IV) could be considered to be a contribution of $HSeO_3^-$ and SeO_3^{2-}[25]. At a low pH value $HSeO_3^-$ would be taken up by the resin and at a high pH value, SeO_3^{2-} would be the species picked up by the resin. It was attempted to theoretically predict the uptake of selenium(IV) at various pH values if the uptakes at two extreme values of pH were known - highly acidic and highly basic.

The resin phase concentration of selenium(IV), q_{Se}, could be viewed as the sum of the contributions of $HSeO_3^-$ and SeO_3^{2-}. Therefore, q_{Se} could be given as,

$$q_{Se} = q_{HSeO_3^-} + q_{SeO_3^{2-}} \qquad 4.1.5$$

For the sake of simplicity, $q_{HSeO_3^-}$ will be referred to as q_I and $q_{SeO_3^{2-}}$ will be referred to as q_{II}. The resin, DOW 2N-Cu, may be represented as $(C_5H_5N)Cu^{2+}$. Thus, two equations can be considered for the uptake of selenium(IV) by DOW 2N-Cu. They are as follows,

$$RSO_4 + 2HSeO_3^- = R(2HSeO_3) + SO_4^{2-} \qquad 4.1.6$$

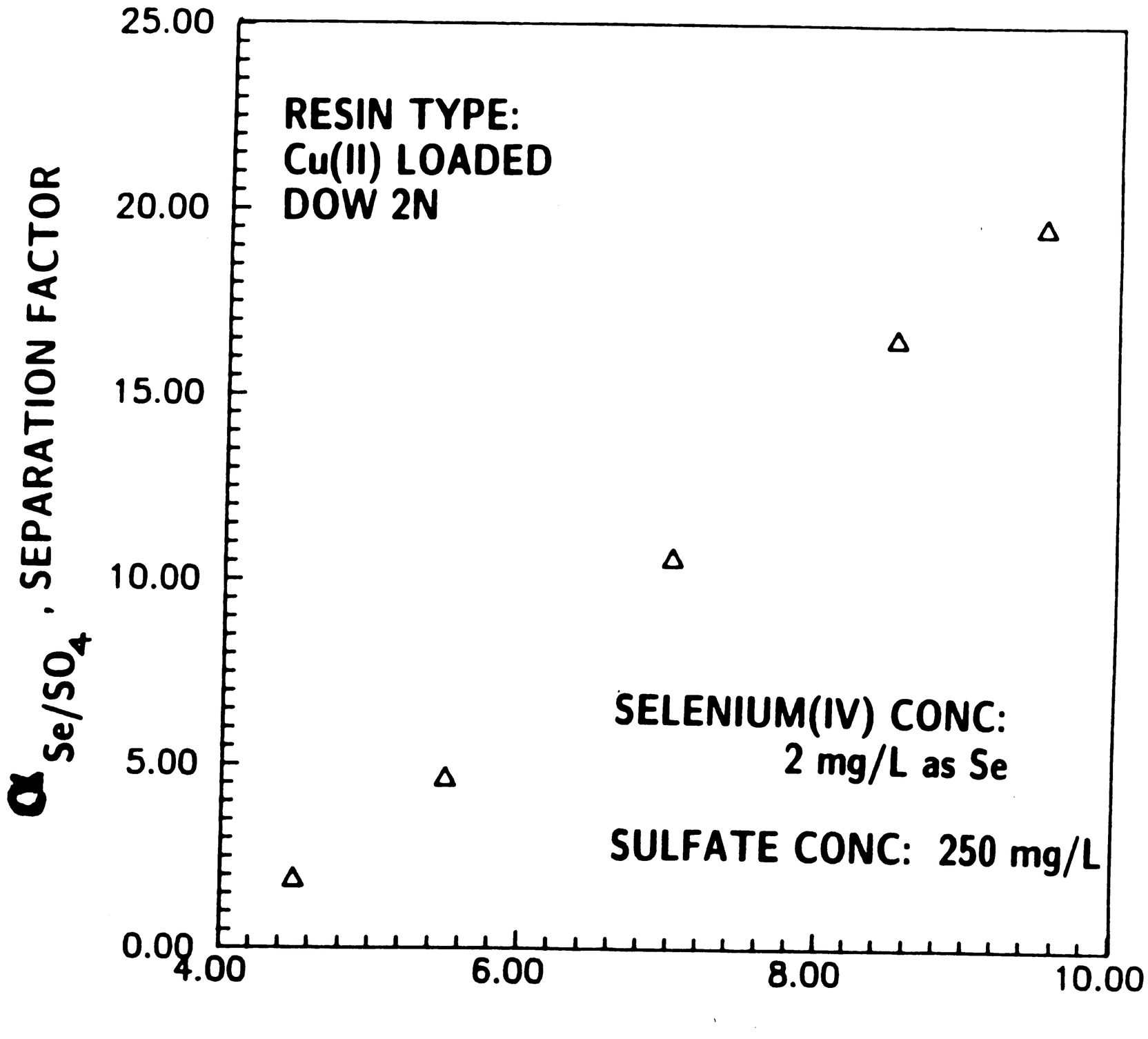


Figure 4-7: Plot Of Separation Factor Vs. pH For Selenite-Sulfate Interchange by DOW 2N-Cu

Serial No.	pH	Resin Phase Se(IV) Conc, q_{Se}, in mg Se/gm Resin	Resin Phase Sulfate Conc, q_{SO_4}, in mg/gm Resin	Separation Factor, $\alpha_{Se/SO_4} = \frac{q_{Se}\,[SO_4]}{[Se]\,q_{SO_4}}$
1	4.50	1.76	115.16	1.91
2	5.50	3.96	106.08	4.67
3	7.00	6.72	79.20	10.60
4	8.50	9.23	69.70	16.55
5	9.50	10.13	64.61	19.60

SELENIUM(IV) CONC: 2 mg/L as Se
SULFATE CONC: 250 mg/L

Table 4-5: Effect of pH on the Selenium-Sulfate Separation Factor For DOW 2N-Cu

$$RSO_4 + SeO_3^{2-} = RSeO_3 + SO_4^{2-} \qquad 4.1.7$$

Please note that R represents the resin phase. The equilibrium constant for equation 4.1.6 may be represented as,

$$K_I = \frac{q_I C_{SO_4}}{q_{SO_4} C_{Se1}^2} \qquad 4.1.8$$

where,

$C_{Se1} = \alpha_1 C_{T,Se}$

q_I= Resin phase concentration of $HSeO_3^-$, in mmole/gm.

C_{SO_4}= Aqueous phase sulfate concentration, in mmole/L.

q_{SO_4}= Resin phase sulfate concentration, in mmole/gm.

$C_{T,Se}$, is the total concentration of selenium(IV) in mmole/L and α_1 is the first ionisation fraction of selenious acid. Thus, C_{Se1}, represents the aqueous phase concentration of $HSeO_3^-$, in mmole/L.

Similarly, for equation 4.1.7, the equilibrium constant may be written as ,

$$K_{II} = \frac{q_{II} C_{SO_4}}{q_{SO_4} C_{Se2}} \qquad 4.1.9$$

Where,

q_{II}= Resin phase concentration of SeO_3^{2-}, in mmole/gm.

C_{SO_4}, $C_{T,Se}$ and q_{SO_4} have the same meanings as stated before.

C_{Se2}=Aqueous phase concentration of SeO_3^{2-} in mmole/L.

$C_{Se2} = \alpha_2 C_{T,Se}$.

Where, α_2 is the second ionisation fraction of selenious acid.

At a low pH value, it can be assumed that the selenium uptake would be due to $HSeO_3^-$. This is because α_2 will be much lower than α_1. At a high pH, α_2

will be much higher than α_1, therefore the selenium(IV) would be taken up as SeO_3^{2-}. At intermediate pH values, the selenium uptake would be a combination of the two species with the contribution of each depending on the pH value.

Therefore, q_{Se} can be given as,

$$q_{Se} = q_I + q_{II} \qquad 4.1.10$$

Where, q_I and q_{II} can be calculated using equation 4.1.8 and equation 4.1.9, respectively. Table 4-6 gives the values of K_I and K_{II}. K_I and K_{II} were computed using equation 4.1.8 and equation 4.1.9, and experimentally determined values of q_I, q_{II} and q_{SO_4} at pH 4.5 and pH 9.5 respectively. Please note that the aqueous phase concentrations of sulfate and selenium(IV) were held constant throughout the experiment at 250 mg/L and 2 mg/L as Se respectively. Table D-1, in Appendix D, tabulates the theoretically predicted values of q_I and q_{II}. The experimentally determined values of q_{Se}, at various pH values, are indicated in Table 4-5. The theoretically predicted values of q_I and q_{II}, were computed at various pH values, using a fixed aqueous concentration of selenium(IV)- 2mg/L as Se. The procedure for the calculations is shown in Appendix D. Figure 4-8 is a graphical representation of the results. As pH increases, the experimental and theoretical values of uptake increase and become equal. At pH values greater than 8.5, the value of q_{Se} becomes almost constant. This is expected because maximum uptake of selenium(IV) should occur at a high pH, since the Lewis Acid-Base interaction will be high when the predominant species is the selenite ion. For a constant aqueous phase selenium(IV) concentration, at a pH much greater than the $pk_{a,2}$ of selenious acid, the speciation remains unchanged with further increase in pH and the selenium(IV) uptake, therefore, should remain constant[25].

The predicted values are lower than the experimental values. This could

Serial No.	pH	α_1	α_2	Aqueous Phase $[HSeO_3^-]$ conc $= \alpha_1 \cdot C_{T,Se}$, in mg/L	Aqueous Phase $[SeO_3^{=}]$ conc, $= \alpha_2 \cdot C_{T,Se}$, in mg/L	Resin Phase Se(IV) Conc, q_{Se}, in mg Se/gm Resin	Resin Phase Sulfate Conc, q_{SO_4}, in mg/gm Resin	K_I	K_{II}
1	4.5	0.992	0.000	1.98	0.02	1.76	115.16	76.62	—
2	9.5	0.025	0.976	0.05	1.95	10.13	64.61	—	20.11

Total Selenium Conc., $C_{T,Se} = 0.0253$ mmole/L.

Sulfate Conc. = 250 mg/L.

Table 4-6: Computation Table For K_I and K_{II}

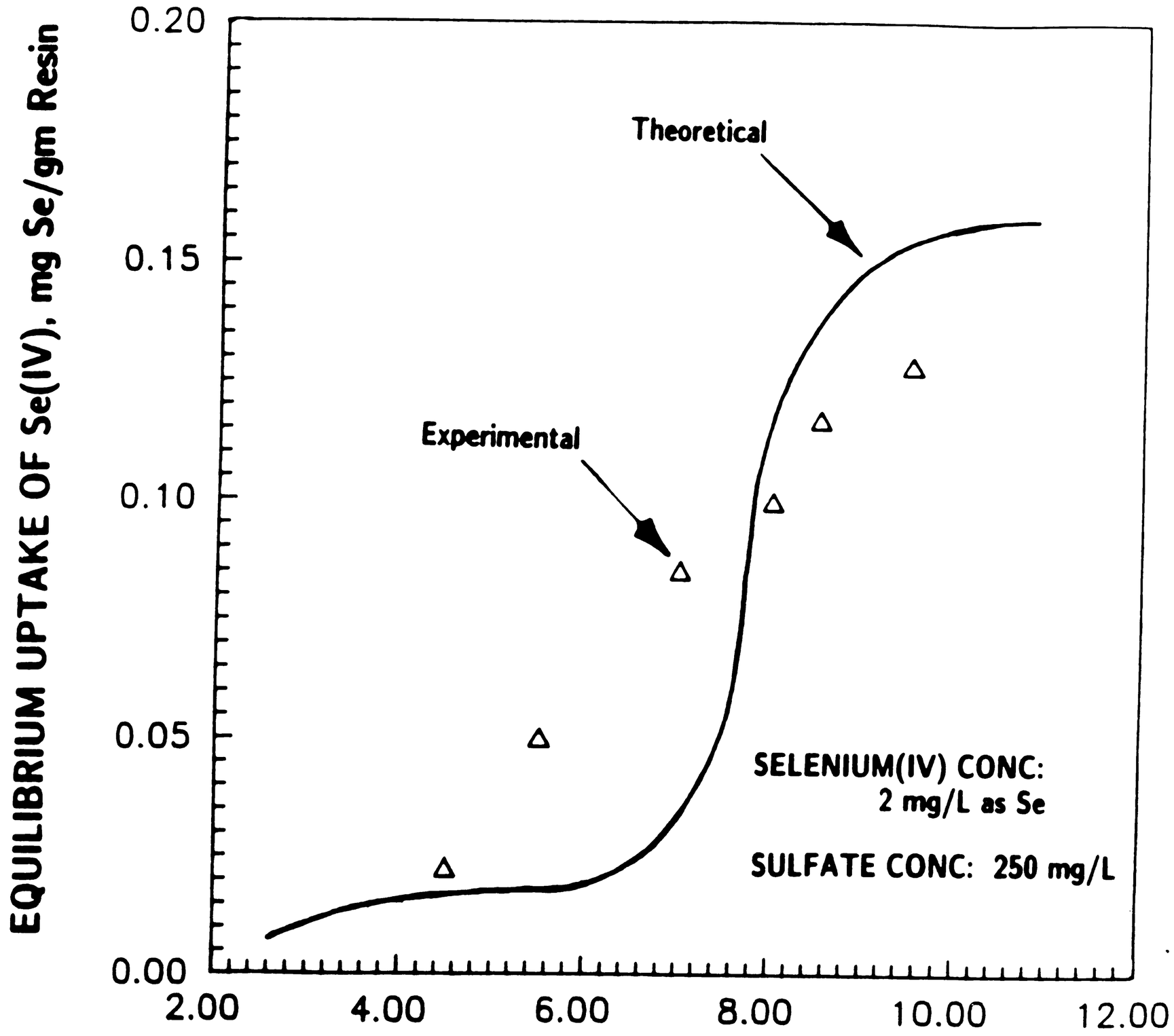


Figure 4-8: Graphical Representation of Experimental and Theoretical Uptake of Selenium At Various pH Values By DOW 2N-Cu

be because the mechanism of uptake is a combination of several effects which cannot be segregated as simply as assumed.

4. COMPARISON WITH OTHER CHELATING EXCHANGERS:

Anion exchange capacity of copper loaded chelating resins should be related to the residual charges on the resin bound cupric ion and the Lewis acid-base interaction between the cupric ion and the aqueous anionic species. The ligand exchange capacity of the Cu^{2+} ion is in turn related to the coordinate valences of the copper atom.

Figure 4-9 and Figure 4-10 indicate that selenite and arsenate uptake by IRC 718 is negligible in comparison to DOW 2N-Cu. Thus confirming that IRC 718, when chelated with copper has negligible anion exchange capacity. This is because the copper atom has no residual charges. Figure 4-11, compares the mechanism of anion uptake by DOW 2N-Cu and copper loaded IRC 718. The possible reason for the low anion exchange capacity of copper loaded IRC 718 is indicated in the figure.

Thus selective uptake of selenite and arsenate by DOW 2N-Cu could be attributed to complex formation, of the aqueous anionic species, with the Cu^{2+} ions (fixed by chelation to the resin matrix). The mechanism involves ligand exchange and Lewis Acid-Base interaction. Presence of unsatisfied coordinate valences of the copper ion is necessary for this type of exchange to occur.

5. COMPARISON OF DOW 2N-Cu AND DOW 3N-Cu

Presence of unsatisfied coordinate valences of the resin-held copper ion is a must for ligand exchange sorption to occur. DOW 3N as stated before has a much higher affinity for the copper atom. This is evident by the higher copper capacity(2.453 meq/gm) of this resin as compared to that of DOW 2N(1.67 meq/gm). However, the copper atom in DOW 3N is chelated to three nitrogen atoms as against the copper atom in DOW 2N, which is chelated to two nitrogen

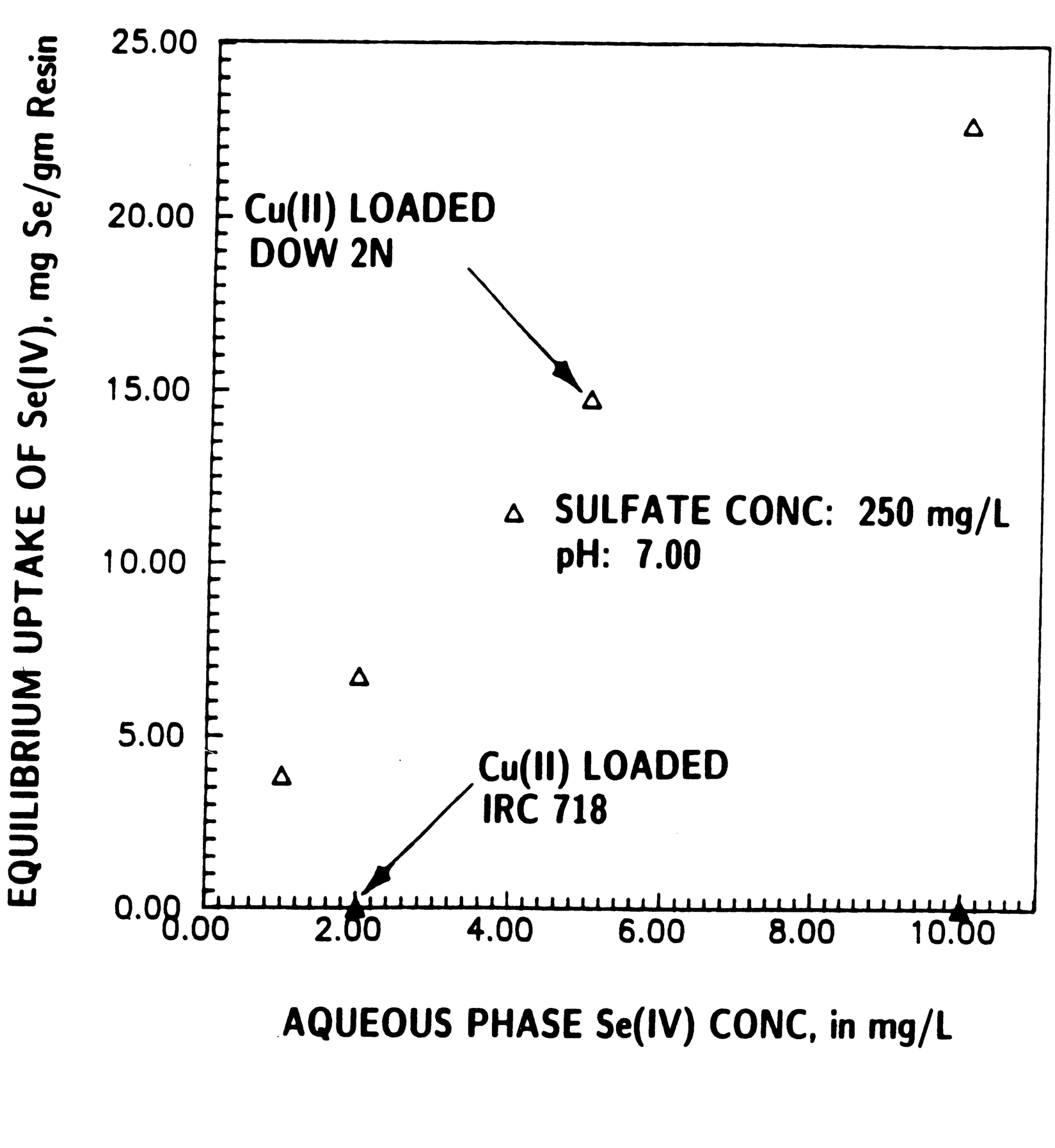


Figure 4-9: Comparison Of Selenite Uptake By DOW 2N-Cu And Copper Loaded IRC 718

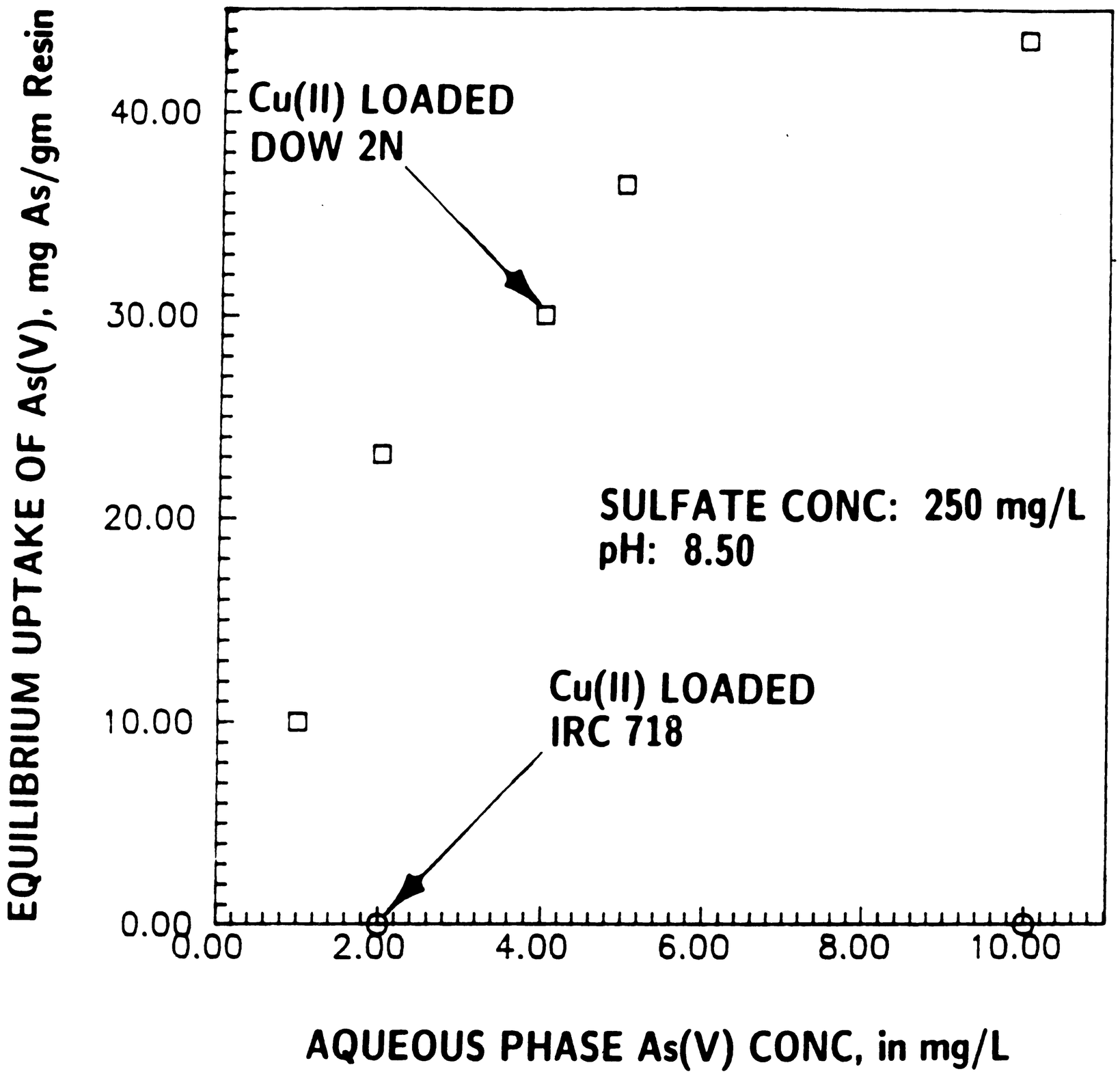
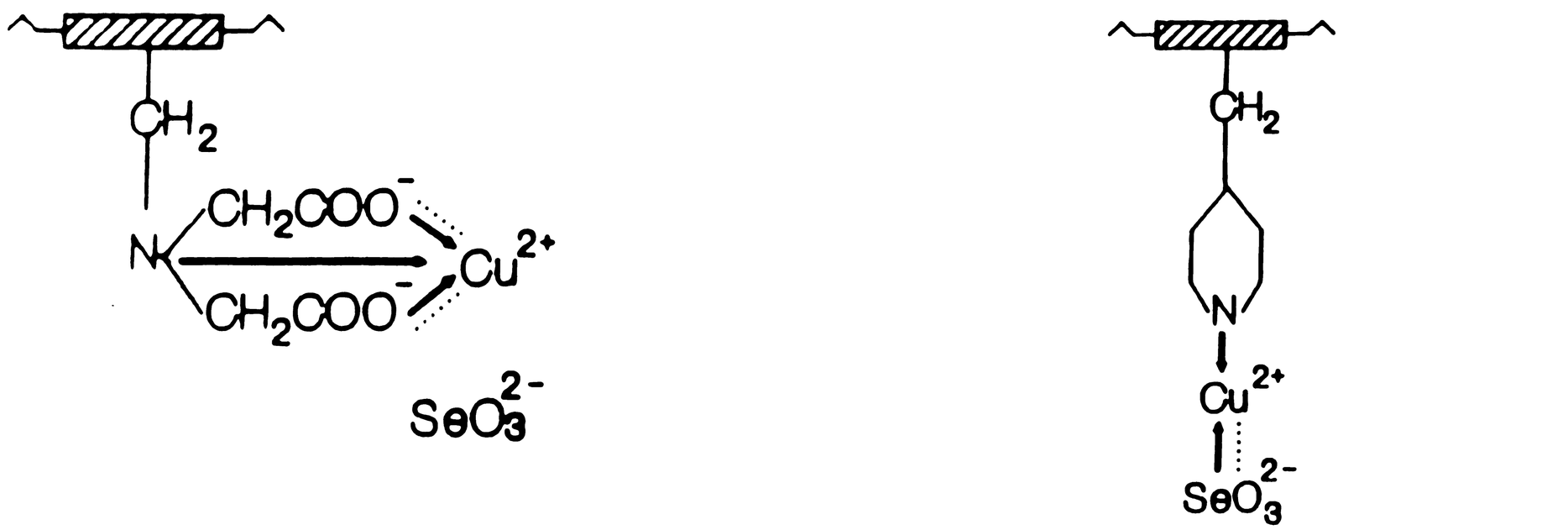


Figure 4-10: Comparison of Arsenate Uptake by DOW 2N-Cu And Copper Loaded IRC 718



Arrows indicate coordinate covalent bonds formed by Lewis acid-base interaction. The fixed negative charges on the iminodiacetate functionality neutralize the positive charges on the copper atom. Thus the copper atom does not have any residual charges. No ion-pair formation can take place between the resin held copper atom and the selenite ion in the aqueous phase.

Figure 4-11: Comparison Of The Mechanism Of Anion Uptake By Copper Loaded IRC 718 and DOW 2N-Cu

atoms. Therefore, the copper atom in DOW 3N has fewer unsatisfied coordinate valences as compared to the copper atom in DOW 2N.

Figure 4-12 compares the arsenate-sulfate separation factor for DOW 2N-Cu and DOW 3N-Cu under identical experimental conditions. A lower separation factor in the case of DOW 3N-Cu can be seen. The arsenate-sulfate separation factor for DOW 3N-Cu is tabulated in Table 4-7. Figure 4-13 compares the selenite uptake by DOW 2N-Cu and DOW 3N-Cu under identical experimental conditions. The selenite-chloride separation factor, for the resin DOW 3N-Cu, is tabulated in Table 4-8. Thus it can be readily seen that anion exchange capacity of DOW 3N-Cu is lower than that of DOW 2N-Cu.

The reason for the lower arsenate and selenite uptake, observed in the case of DOW 3N-Cu, could be explained in terms of the free energy of formation of the complex between the resin bound Cu^{2+}(for DOW 3N-Cu) and the SeO_3^{2-} ion. If the free energy of formation of this compound can be shown to be more than the corresponding complex for DOW 2N-Cu, it can explain the lower selectivity observed in the case of DOW 3N-Cu. It was attempted to prove this by calculations indicated in Appendix B. Some simplifying assumptions were made. However, it was proved that the complex between the resin bound Cu^{2+} and the SeO_3^{2-} ion will be formed more readily in the case of DOW 2N-Cu, due to a corresponding lower free energy of formation, explaining the higher anion selectivity observed in the case of DOW 2N-Cu. Figure 4-14 illustrates the lower anion exchange capacity of DOW 3N-Cu, as compared to that of DOW 2N-Cu, in terms of the coordination valences of the copper atom. Please note that the copper atom is assumed to be chelated only to the pyridine nitrogen atoms.

A column run was carried out using DOW 3N-Cu. Breakthrough of selenium(IV) occurred very early - almost immediately after chloride. Please note that selenium(IV) and chloride have not been shown in the figure. Uptake

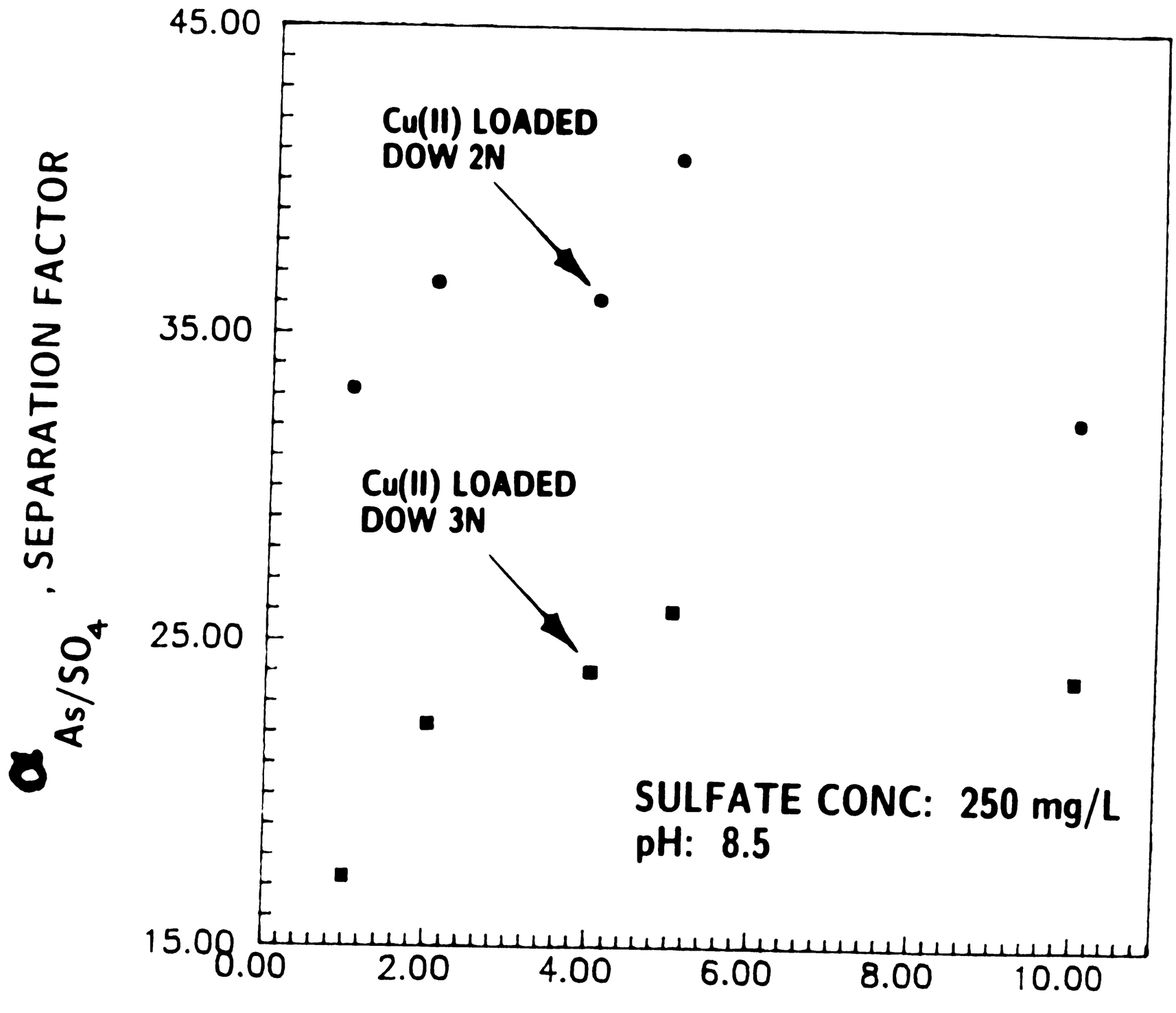


Figure 4-12: Comparison Of The Arsenate-Sulfate Separation Factor For DOW 2N-Cu And DOW 3N-Cu

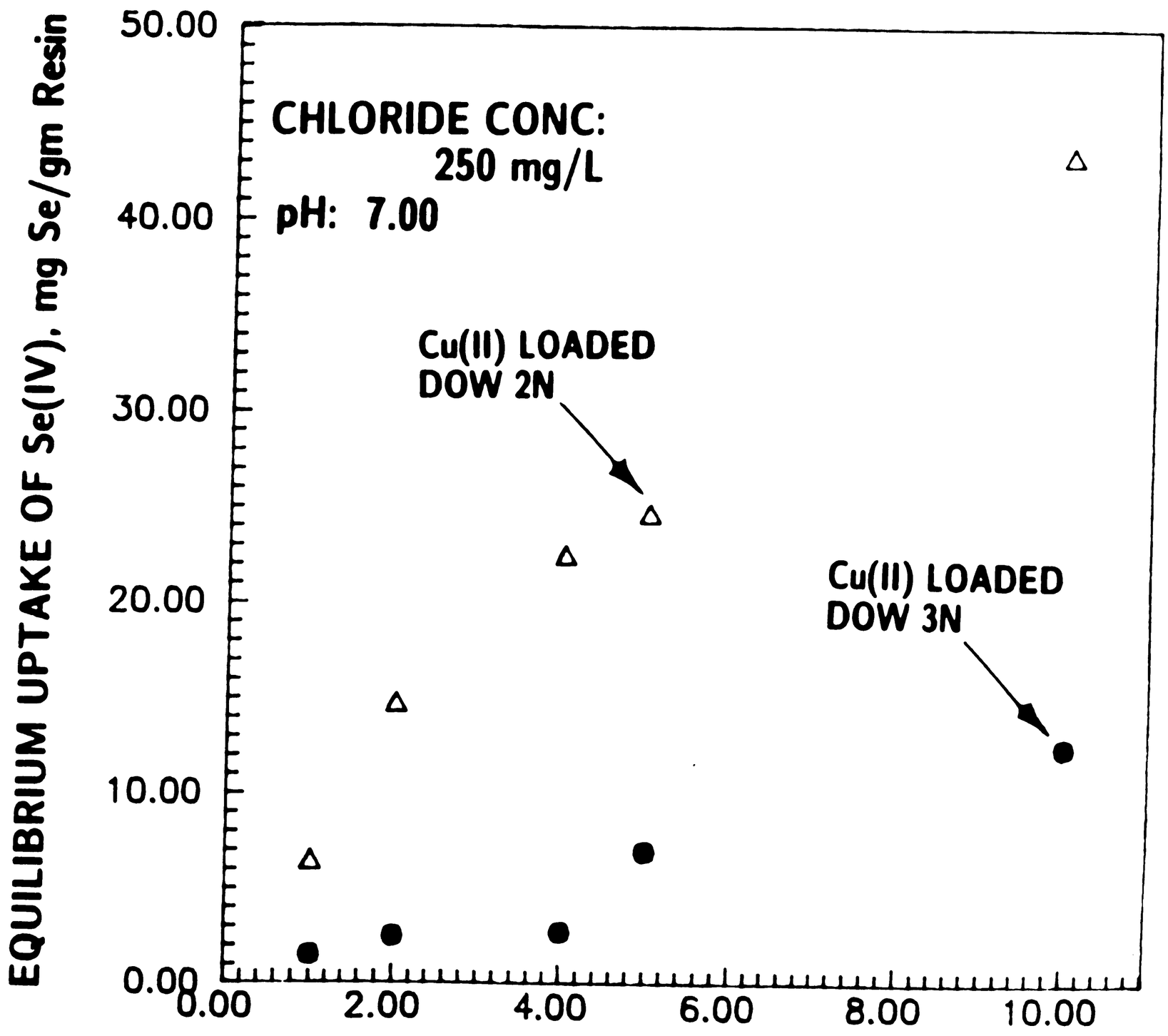


Figure 4-13: Comparison Of Selenite Uptake By DOW 2N-Cu And DOW 3N-Cu

Serial No.	Aqueous Phase As(V) Conc, [As], in mg/L as As	Aqueous Phase Sulfate Conc, $[SO_4^{2-}]$, in mg/L	Resin Phase As(V) Conc, q_{As}, in mg/gm Resin	Resin Phase Sulfate Conc, q_{SO_4}, in mg/gm Resin	Separation Factor, $\alpha_{As/SO_4} = \frac{q_{As}\,[SO_4]}{[As]\,q_{SO_4}}$
1	1.00	250	7.50	108.84	17.63
2	2.00	250	15.50	86.94	22.27
3	4.00	250	29.20	76.00	24.00
4	5.00	250	37.50	72.11	25.99
5	10.00	250	50.50	52.93	23.85

Table 4-7: Arsenate-Sulfate Separation Factor For DOW 3N-Cu At pH 8.5

Serial No.	Aqueous Phase Se(IV) Conc, [Se], in mg/L as Se	Aqueous Phase Chloride Conc, [Cl^-], in mg/L	Resin Phase Se(IV) Conc, q_{Se}, in mg Se/gm Resin	Resin Phase Chloride Conc, q_{Cl}, in mg/gm Resin	Separation Factor, $\alpha_{Se/Cl} = \frac{q_{Se}\,[Cl]}{[Se]\,q_{Cl}}$
1	1.00	250	1.50	66.05	5.63
2	2.00	250	2.50	57.04	5.49
3	4.00	250	2.74	47.55	3.60
4	5.00	250	6.98	50.55	6.90
5	10.00	250	12.55	46.75	6.71

Table 4-8: Selenite-Chloride Separation Factor For DOW 3N-Cu At pH 7.00

of arsenate was much higher. From Figure 4-15, it can be seen that arsenate breakthrough occurred much later than sulfate. This supports the arsenate-sulfate separation factor(around 25) determined by equilibrium studies. By experiment, DOW 2N-Cu was determined to be a more effective sorbent than DOW 3N-Cu for arsenate and selenite removal.

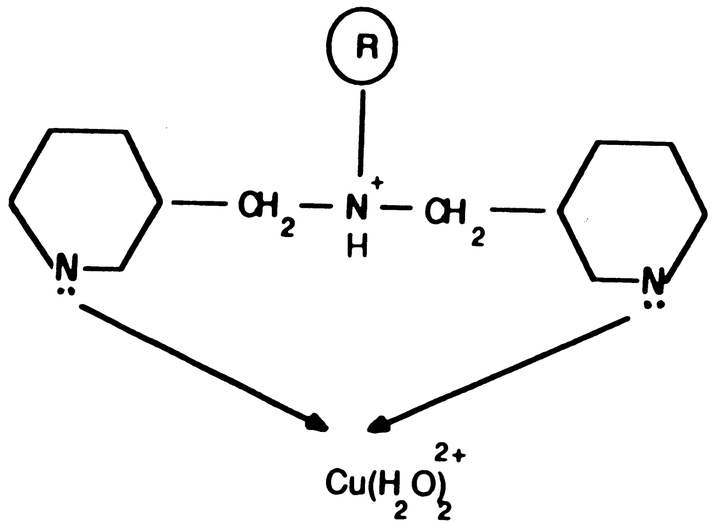
6. REGENERABILITY OF THE EXHAUSTED EXCHANGERS

DOW 2N-Cu used in the column run was regenerated using 2% Ammonia, upon exhaustion. The composition of the influent used to exhaust the resin was: 2 mg/L selenium(VI) as Se, 2 mg/L of selenium(IV) as Se, 100 mg/L sulfate and 200 mg/L chloride. The spent regenerant samples were collected and analysed for the various species. The composition of the influent used to exhaust DOW 3N-Cu was: 2 mg/L selenium(IV) as Se, 2 mg/L selenium(VI) as Se, 2mg/L arsenic(V) as As, 100 mg/L sulfate and 200 mg/L chloride.

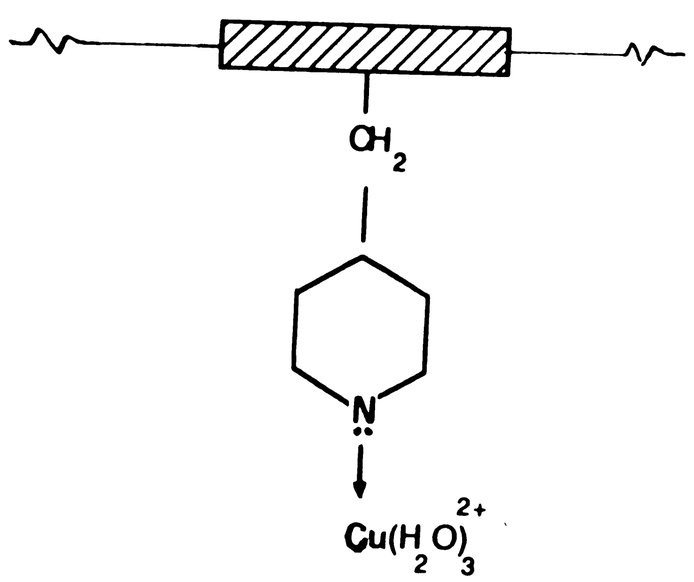
Figure 4-16 and Figure 4-17 show the concentration of selenite and copper in the spent regenerant samples. Less than three bed volumes were sufficient for the complete removal of selenium(IV) from the bed. Mass balance calculations accounted for more than 80 percent of the selenium(IV) on the bed. Thus regeneration of the exhausted bed with 2% ammonia is very efficient. Figure 4-18 is a composite regeneration plot. It indicates the concentration of the anionic species: sulfate, selenite and selenate, in the spent regenerant, on a semi-log plot. Ammonia removes copper from the bed and consequently all the anionic species are removed. This is because the anion exchange capacity of the copper loaded resin is lost once the copper is removed.

In the case of the column run with DOW 3N-Cu, the spent sorbent was also regenerated using 2% Ammonia. Only arsenic(V) and copper have been plotted because they were present in appreciable concentrations in the spent regenerant. Uptake of arsenic(V) was higher than that of the other species. The

DOW 3N-Cu



DOW 2N-Cu



Lower anion uptake is due to fewer coordination valences of the resin-held copper atom, leading to reduced Lewis acid-base interaction.

⟶ Lewis Acid-Base Interaction

Figure 4-14: Mechanism Of Anion Uptake By DOW 2N-Cu And DOW 3N-Cu

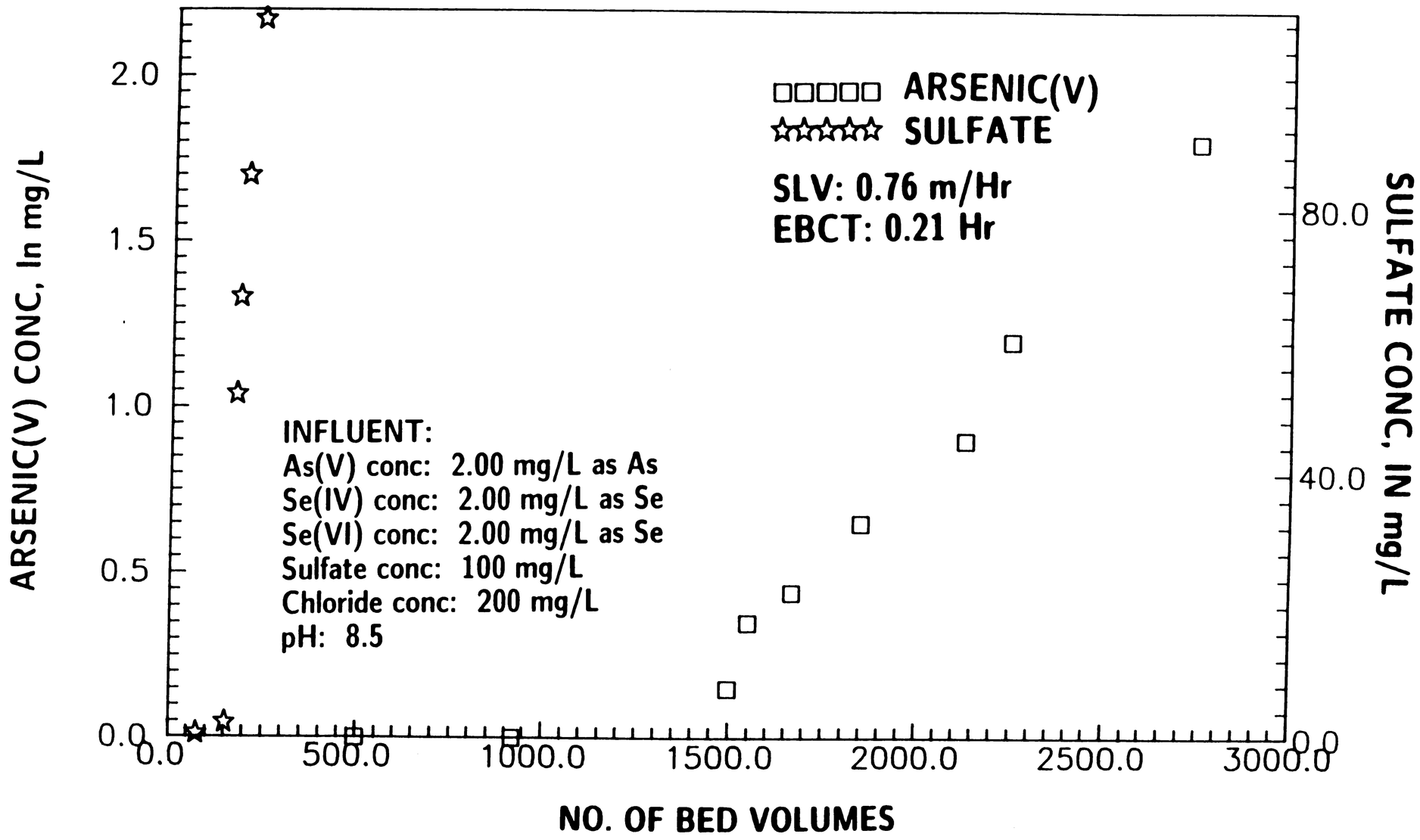


Figure 4-15: Effluent History Plot For The Column Test Using DOW 3N-Cu

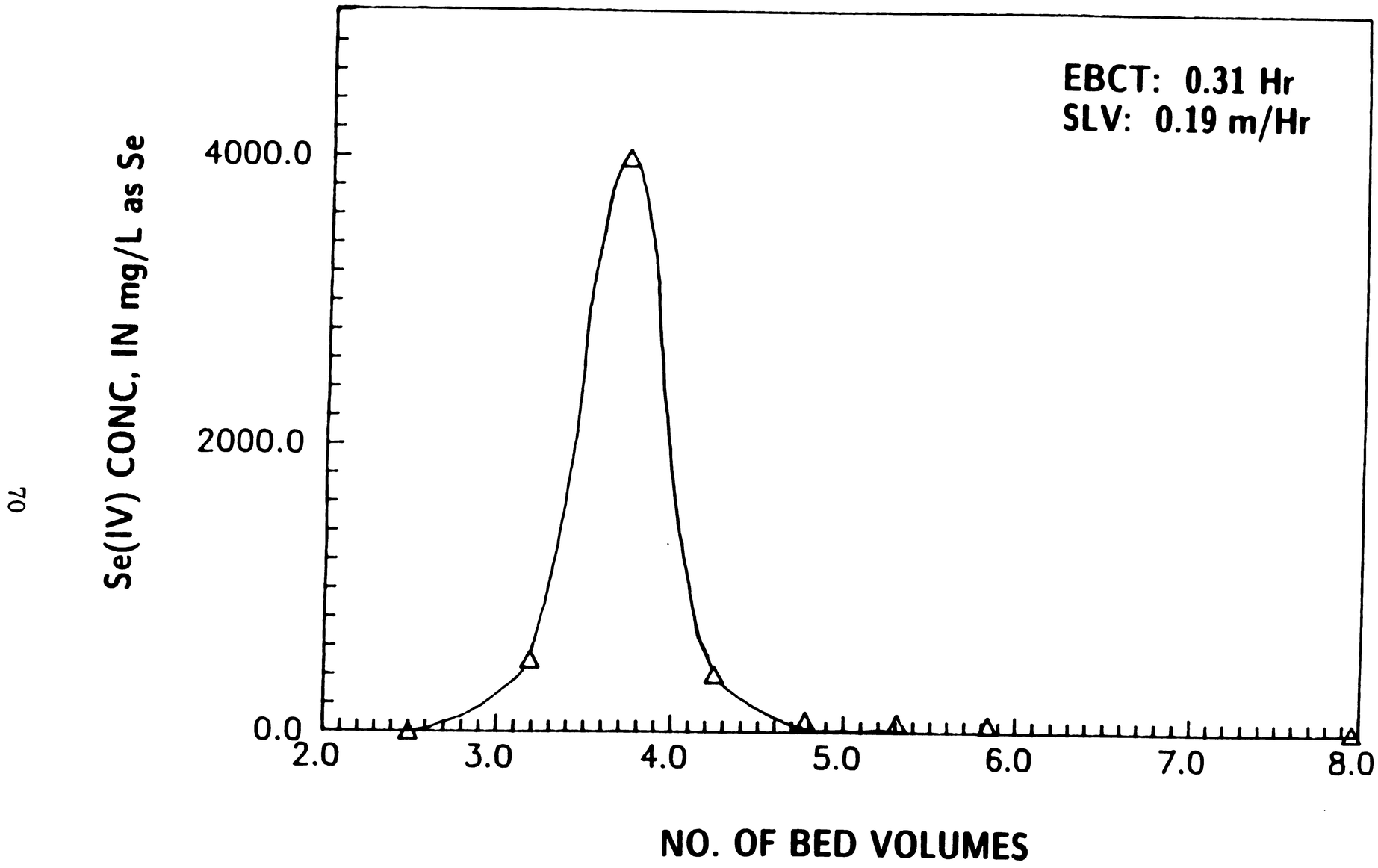


Figure 4-16: Regeneration Plot For DOW 2N-Cu With 2% Ammonia

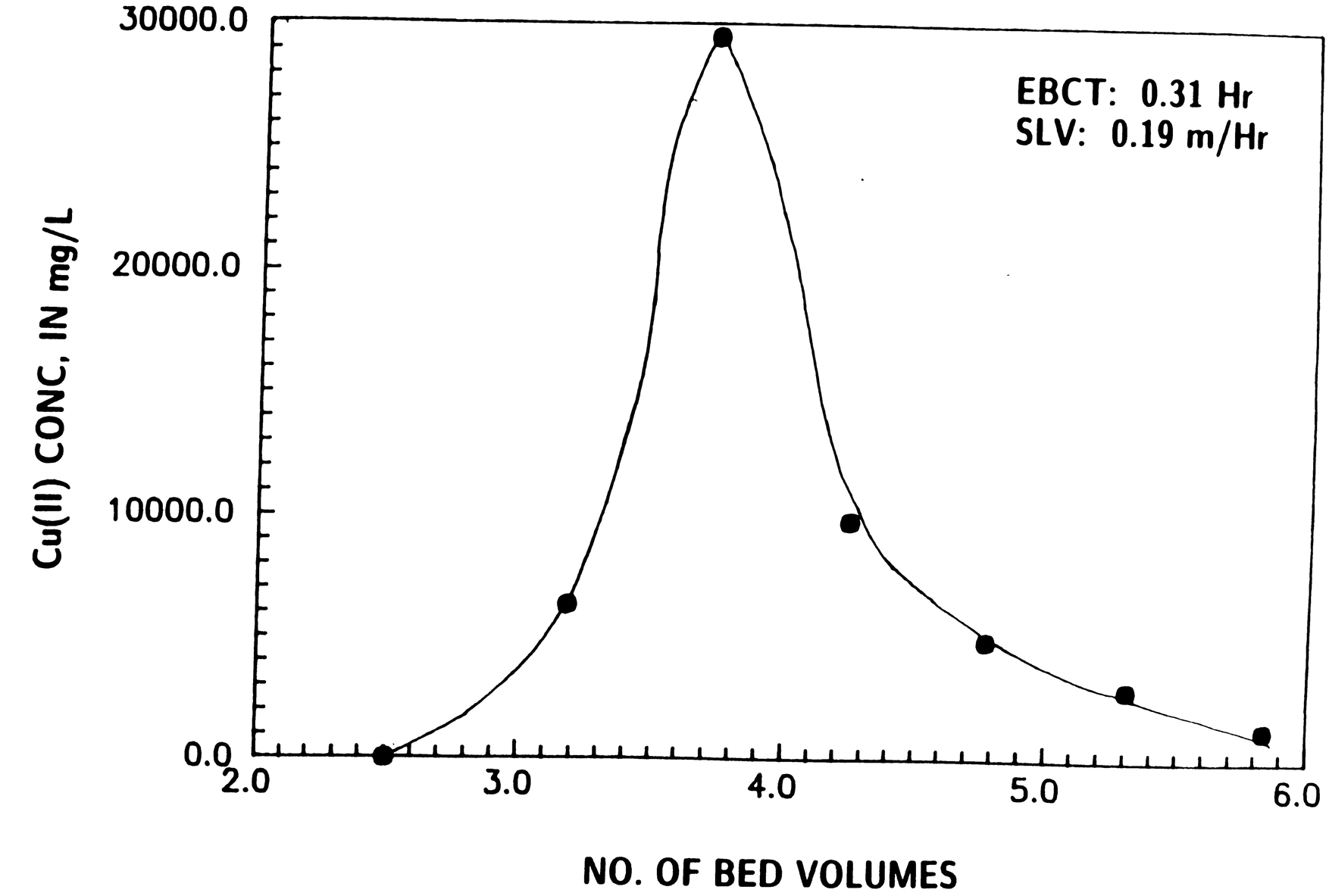


Figure 4-17: Regeneration Plot For DOW 2N-Cu With 2% Ammonia

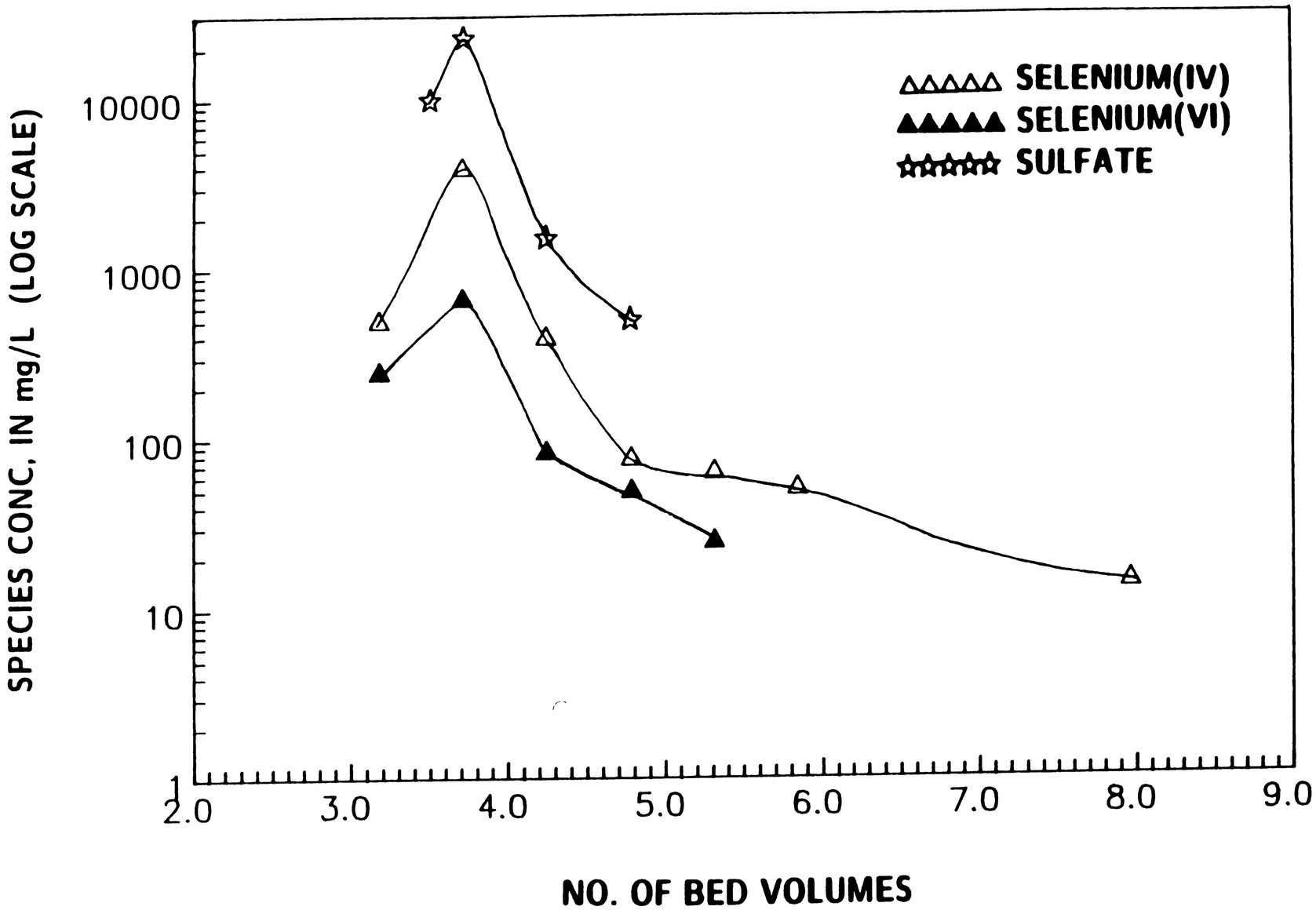
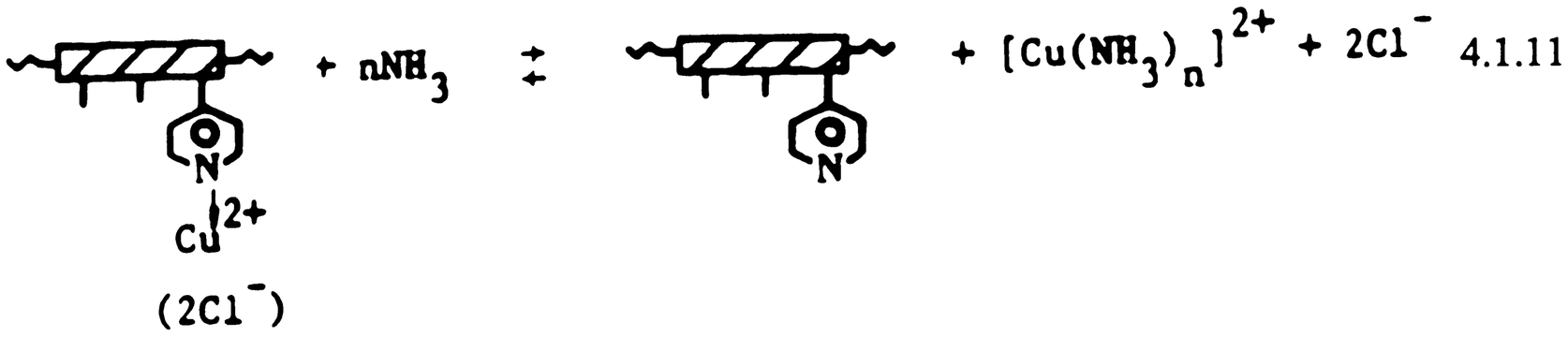


Figure 4-18: Composite Regeneration Plot For DOW 2N-Cu With 2% Ammonia

plots are shown in Figure 4-19 and Figure 4-20.

Regeneration of the copper loaded resins, with ammonia, could be represented by the following reaction:



4.1.11

The forward reaction is favored by the law of mass action at a high ammonia concentration. Thus regeneration is effected by Lewis Acid-Base interaction(or complexation) between the resin-held copper and ammonia(which acts as a ligand).

6. BLEEDING OF COPPER DURING COLUMN RUNS

The copper affinity of DOW 3N is expected to be much higher than that of DOW 2N. This is because the copper atom is chelated to three nitrogen atoms in the case of DOW 3N-Cu, as opposed to two in the case of DOW 2N-Cu. This was checked by placing 2.5 cm of IRC 718 in the column below the copper loaded resins before the start of the respective column runs. Glass wool was used as the separating medium. At the end of the column runs, the IRC 718 was regenerated using 2% hydrochloric acid. For the column run with DOW 3N-Cu, the total copper leakage was determined to be 5.45 mg - the average rate of

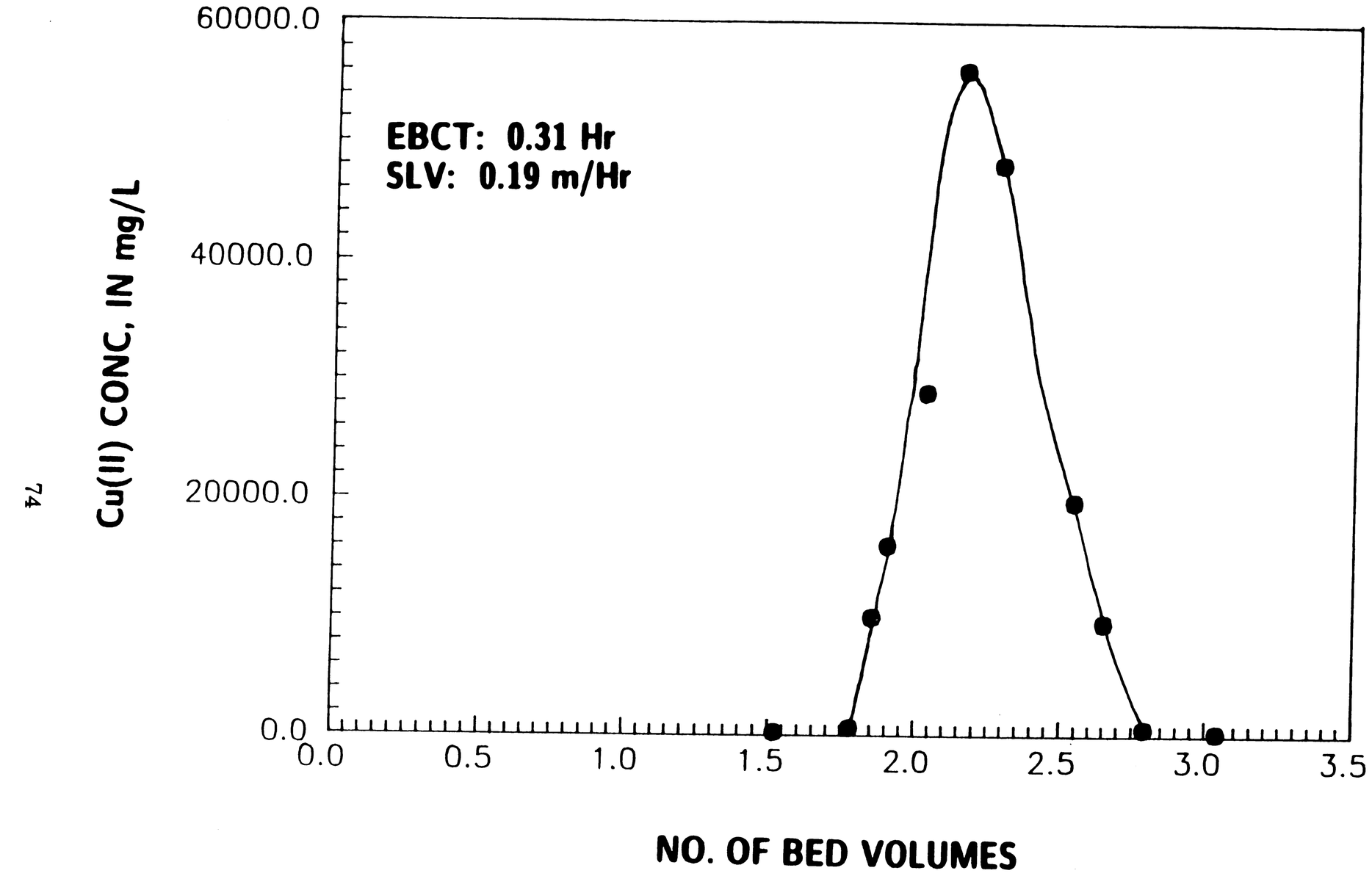


Figure 4-19: Regeneration Plot For DOW 3N-Cu With 2% Ammonia

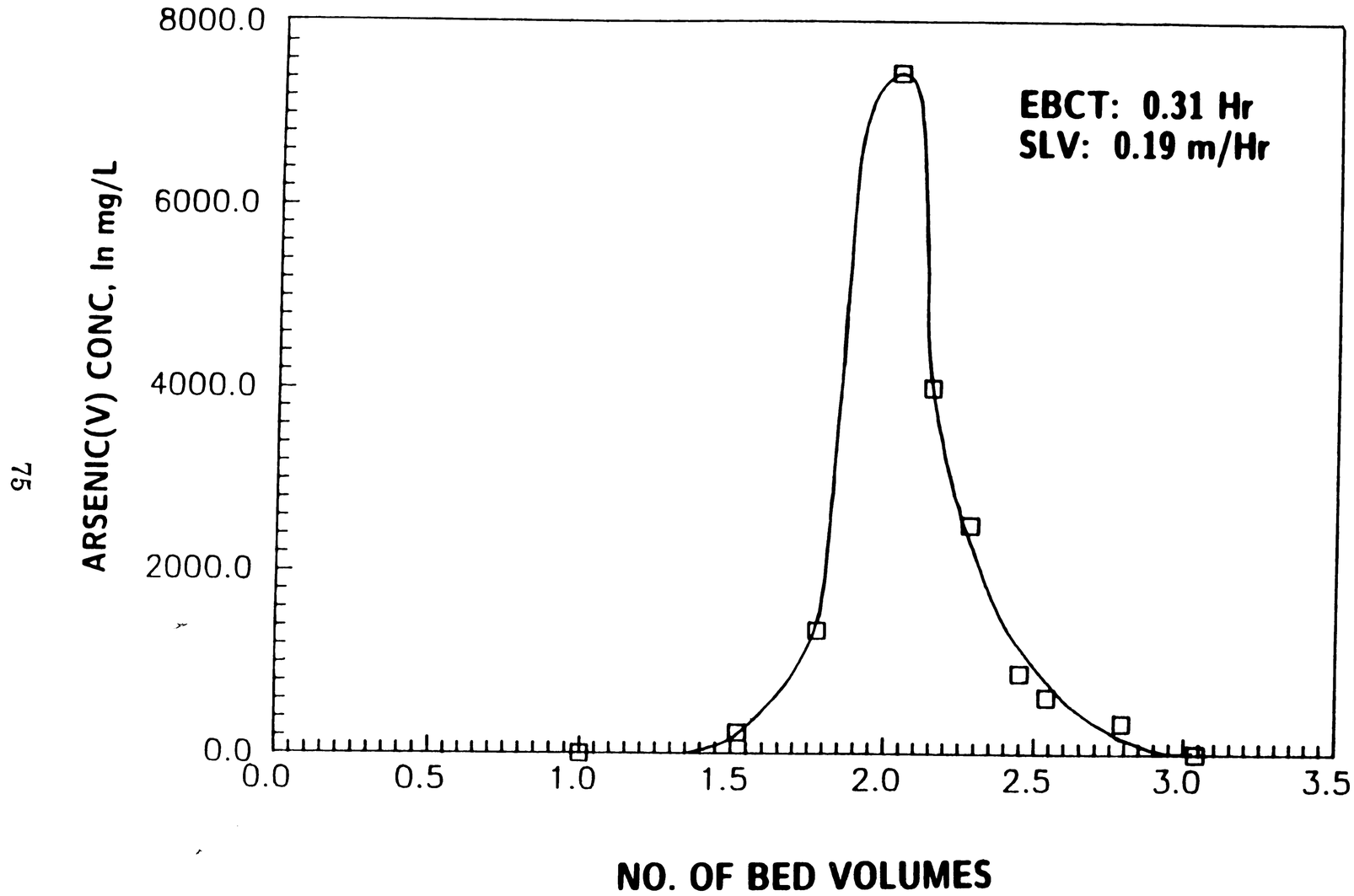


Figure 4-20: Regeneration Plot For DOW 3N-Cu With 2% Ammonia

bleeding was estimated to be 2.2 ug per bed volume of resin. In the run with DOW 2N-Cu, the total copper that leached from the bed was determined to be 79.5 mg - the average rate of bleeding was estimated to be 38.7 ug per resin bed volume. This clearly indicates that DOW 3N binds copper more strongly than DOW 2N. However, equilibrium isotherm tests showed that DOW 3N-Cu has lower anion exchange capacity than DOW 2N-Cu. The reason for the lower anion exchange capacity of DOW 3N-Cu was discussed earlier.

To avoid the bleeding of copper, if this method is used to treat arsenic and selenium contaminated water, the set-up in Figure 4-21 could be used. Virgin IRC-718 could be placed below the copper loaded chelating resin. Glass wool could be used to separate the two resins. The IRC-718 would adsorb any copper bleeding from the DOW 2N-Cu(sorbent used in the process).

7. LOW pH OF THE EFFLUENT SAMPLES

The pH of the influent, used to exhaust the resin(DOW 2N-Cu), was 9.5. The effluent history of the column run, using this sorbent is indicated in Figure 4-4. However, the pH of the effluent samples was low. The variation of the effluent pH, from the start of the column run until exhaustion of the resin bed, is indicated in Figure 4-22. The hydroxyl ion is a competing ligand and can also be taken up by the resin. This would explain the consistently low pH of the column effluent, throughout the run.

4.2 SHORTCOMINGS AND CORRECTIVE MEASURES

From the results presented earlier, it follows that any ligand that forms a stronger complex(high formation constant) with copper would reduce the uptake of arsenate and selenite. This is because the mechanism of anion uptake involves Lewis acid-base interaction. $CuCO_3$ has a very low solubility product(or a very high formation constant). K_{sp} for $CuCO_3 = 1.4\times10^{-10}$.

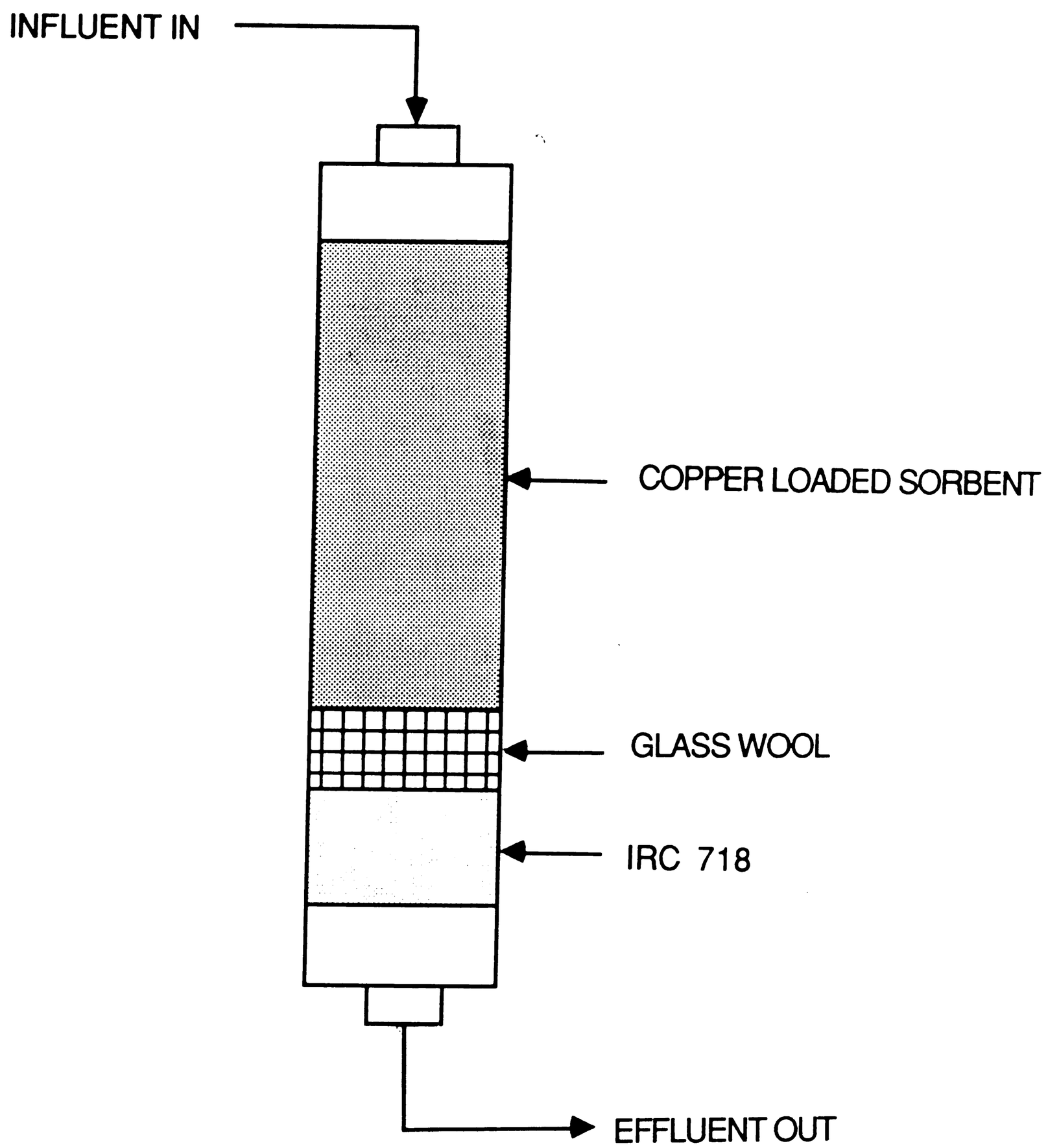


Figure 4-21: Set Up To Prevent Copper Bleeding In the Proposed Treatment Method

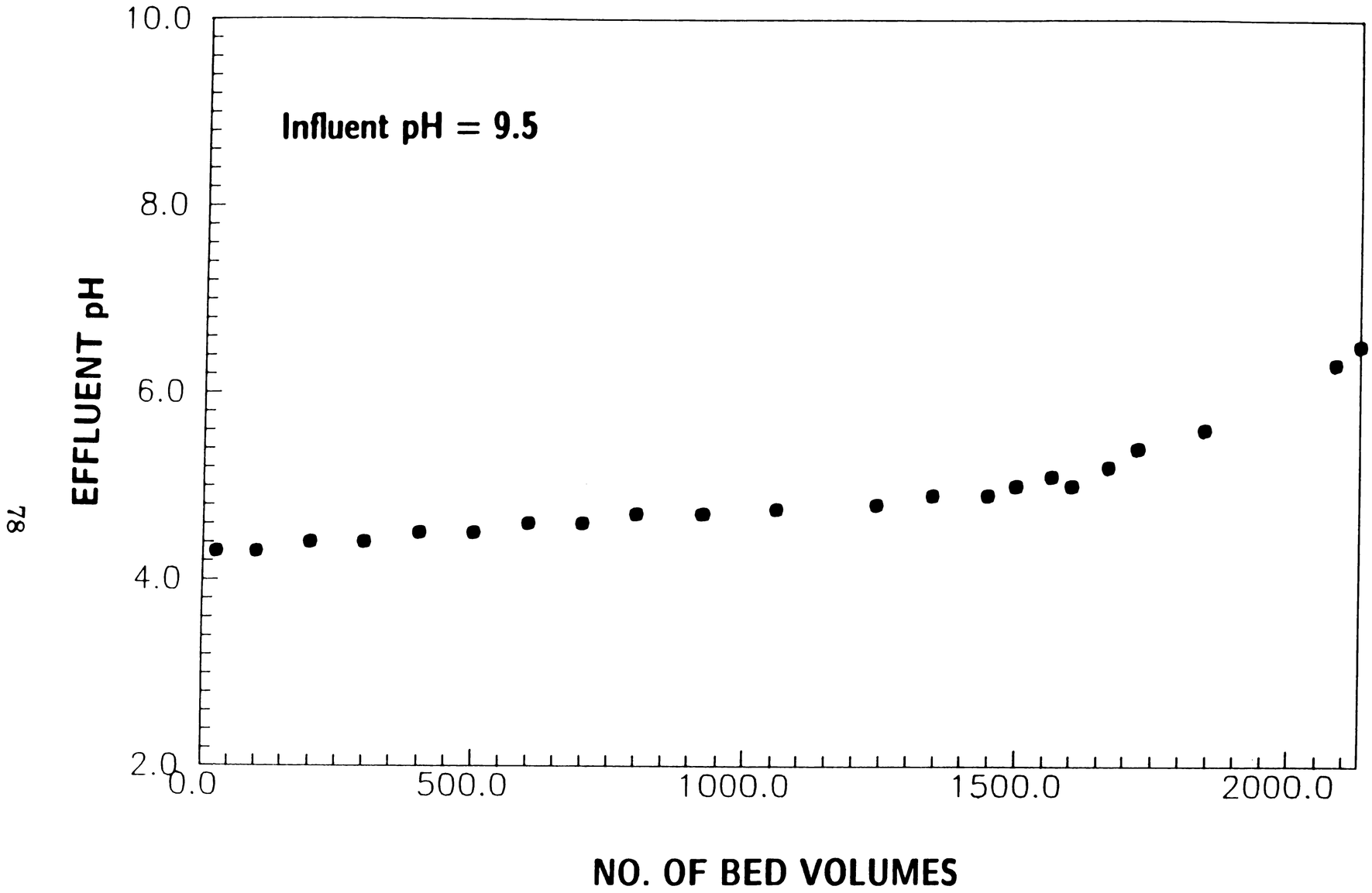


Figure 4-22: Effuent pH Variation During Column Run With DOW 2N-Cu As Sorbent

Carbonate ions when present, would therefore act as competing ligands, reducing the uptake of selenite and arsenate.

Studies were conducted to determine the effect of bicarbonate on the uptake of arsenate and selenite. Figure 4-23 shows the uptake of selenite in the presence of bicarbonate. At pH 8.5, the predominant species would be the bicarbonate ion, HCO_3^-. The experiment was conducted at pH 8.5 and the competing ion(bicarbonate) concentration was held constant at 200 mg/L. Low separation factors, as shown in Table 4-9, indicate that bicarbonate significantly reduces the uptake of the selenite ion. Please note that all calculations were done in terms of bicarbonate, which was estimated by titration.

pH should also have a significant effect on the uptake of the selenite and arsenate in the presence of bicarbonate. As the pH increases, the fraction of total carbonate($C_{T,C}$) present as carbonate, will increase and the uptake of carbonate would increase, thereby reducing the uptake of arsenate and selenite. Figure 4-24 shows the effect of pH on the uptake of arsenate in the presence of bicarbonate. The arsenate-bicarbonate separation factor, at different pH values, is tabulated in Table 4-10. Similarly, Figure 4-25 shows the effect of pH on the selenite uptake, by DOW 2N-Cu, in the presence of bicarbonate. Table 4-11, gives the selenite-bicarbonate separation factor, at various pH values. All calculations were done in terms of total carbon. The experiments were conducted at a fixed aqueous phase concentration of arsenate and/or selenite, in the presence of a constant, competing, bicarbonate concentration of 200 mg/L(total carbon concentration of 39.34 mg/L). On the same figures the ratios of the second ionization fraction of arsenic acid($\beta_{2,As}$) and/or that of selenious acid($\beta_{2,Se}$) to the second ionization fraction of carbonic acid($\beta_{2,C}$) have been superimposed. For the most part, uptake of arsenic(V) follows the same trend as $\beta_{2,As}/\beta_{2,C}$. Uptake of selenium(IV) follows the same trend as $\beta_{2,Se}/\beta_{2,C}$.

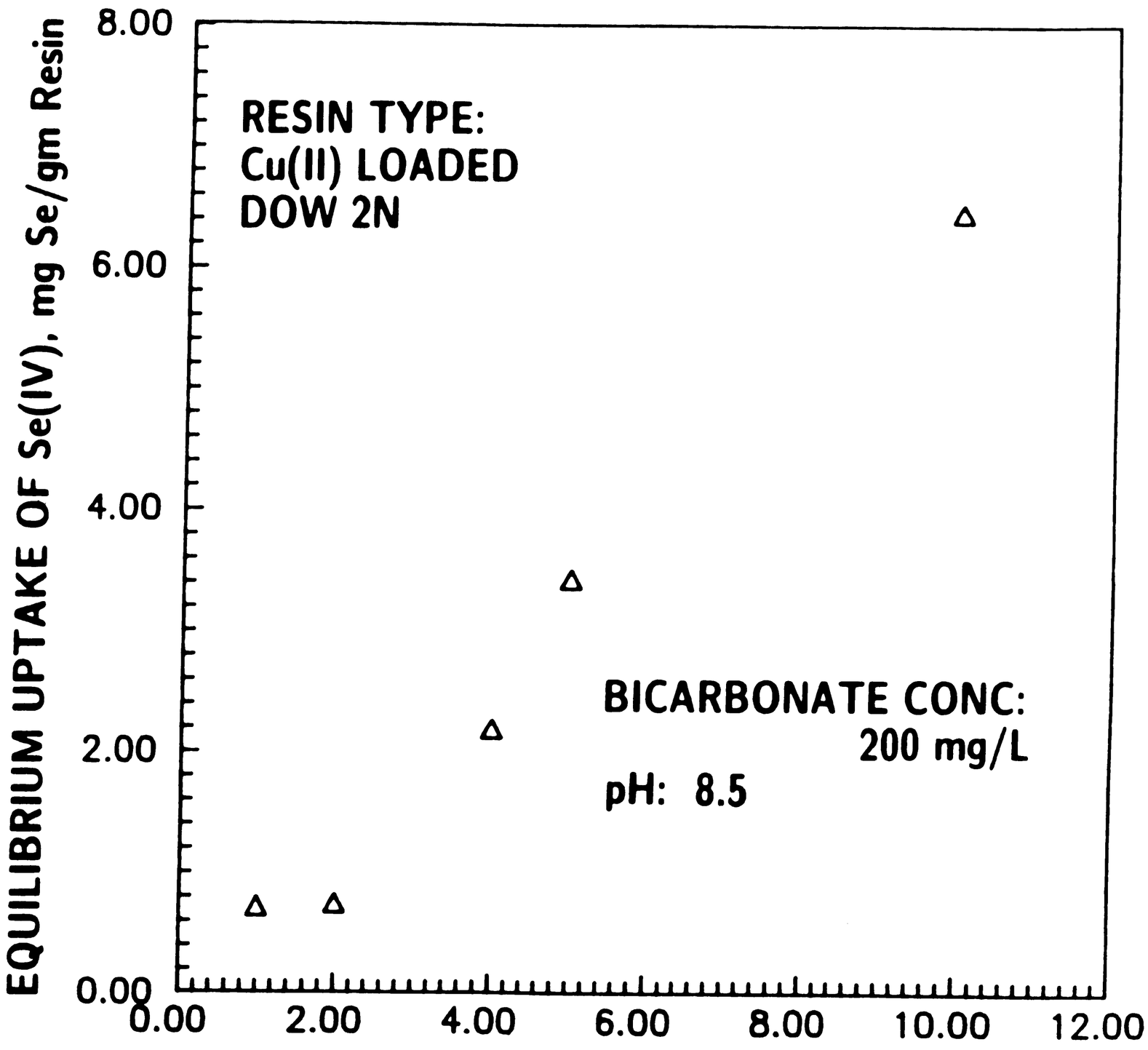


Figure 4-23: Selenite-Bicarbonate Isotherm For DOW 2N-Cu At pH 8.5

Serial No.	Aqueous Phase Se(IV) Conc, [Se], in mg/L as Se	Aqueous Phase Bicarbonate Conc, $[HCO_3^-]$, in mg/L	Resin Phase Se(IV) Conc, q_{Se}, in mg Se/gm Resin	Resin Phase Bicarbonate Conc, $q_{HCO_3^-}$, in mg/gm Resin	Separation Factor, $\alpha_{Se/HCO_3} = \frac{q_{Se}\,[HCO_3^-]}{[Se]\,q_{HCO_3}}$
1	1.00	200	0.71	1342	0.11
2	2.00	200	0.74	1268.8	0.06
3	4.00	200	2.19	1134.6	0.10
4	5.00	200	3.43	1207.8	0.11
5	10.00	200	6.46	1073.6	0.12

Table 4-9: Selenite-Bicarbonate Separation Factor For DOW 2N-Cu At pH 8.5

Where As represents arsenic acid, Se selenious acid and C carbonic acid. Please note that the variation of the earlier specified ratios is indicated on the figures by a solid line. The deviation of the first data point in the case of arsenic(V) could be due to experimental error. No explanation could be provided for it. Please see Appendix C for a more complete definition of the various ionization fractions.

Groundwaters are most often found contaminated with trace concentrations of arsenic and selenium. Therefore, this selective process would be useful in such a situation. However, they are also characterized by the presence of high carbonate concentrations. Thus the application of this removal technique would require stripping the water of all carbonate. A schematic of the proposed method of treatment, of high carbonate waters, in shown in Figure 4-26.

4.3 APPLICATIONS OF THE METHOD- SULFIDE REMOVAL

From the foregoing discussion, any species which forms a copper compound with a high formation or stability constant could be a target for removal, if this method were to be employed. Cupric Sulfide has a high formation constant, as indicated in Table 2-1. Thus the sulfide ion should be removed very efficiently by the copper loaded synthetic sorbent(DOW 2N-Cu). Figure 4-27 is the isotherm for sulfide uptake, using DOW 2N-Cu as the sorbent. A high competing ion(sulfate) concentration of 500 ppm was used. The pH was maintained at 10.0 to prevent volatilization of sulfide. High uptake of sulfide can be readily observed. The sulfide-sulfate separation factor for DOW 2N-Cu, was determined to be around 38. Please note that this was at a pH when the predominant aqueous species is HS^- or the bisulfide ion. The separation factors are presented in Table 4-12. An experiment was also

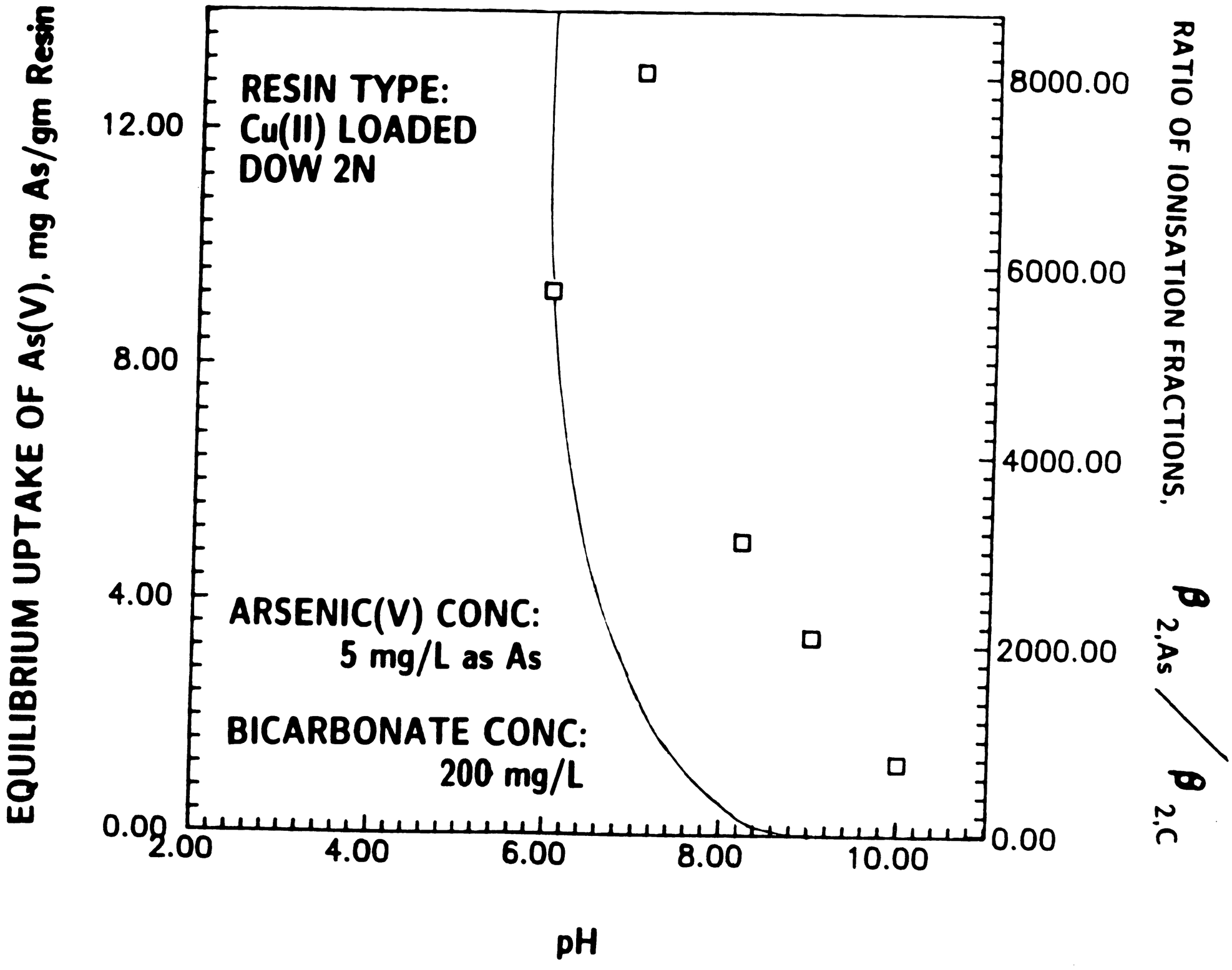


Figure 4-24: Uptake Of Arsenate In The Presence Of Bicarbonate At Various pH Values

Serial No.	pH	Resin Phase As(V) Conc, q_{As}, in mg/gm Resin	Resin Phase Carbon conc, q_C, in mg/gm Resin	Separation Factor, $\alpha_{As/C} = \frac{q_{As}\,[C]}{[As]\,q_C}$
1	6.0	9.26	247.75	0.29
2	7.0	12.98	122.88	0.84
3	8.2	5.02	176.71	0.23
4	9.0	3.39	198.11	0.14
5	10.0	1.24	196.91	0.05

Aqueous phase As(V) conc = 5 mg/L as As

Total Bicarbonate conc = 200 mg/L
Total Carbon conc = 39.34 mg/L

Table 4-10: Effect Of pH On The Arsenate-Bicarbonate Separation Factor For DOW 2N-Cu

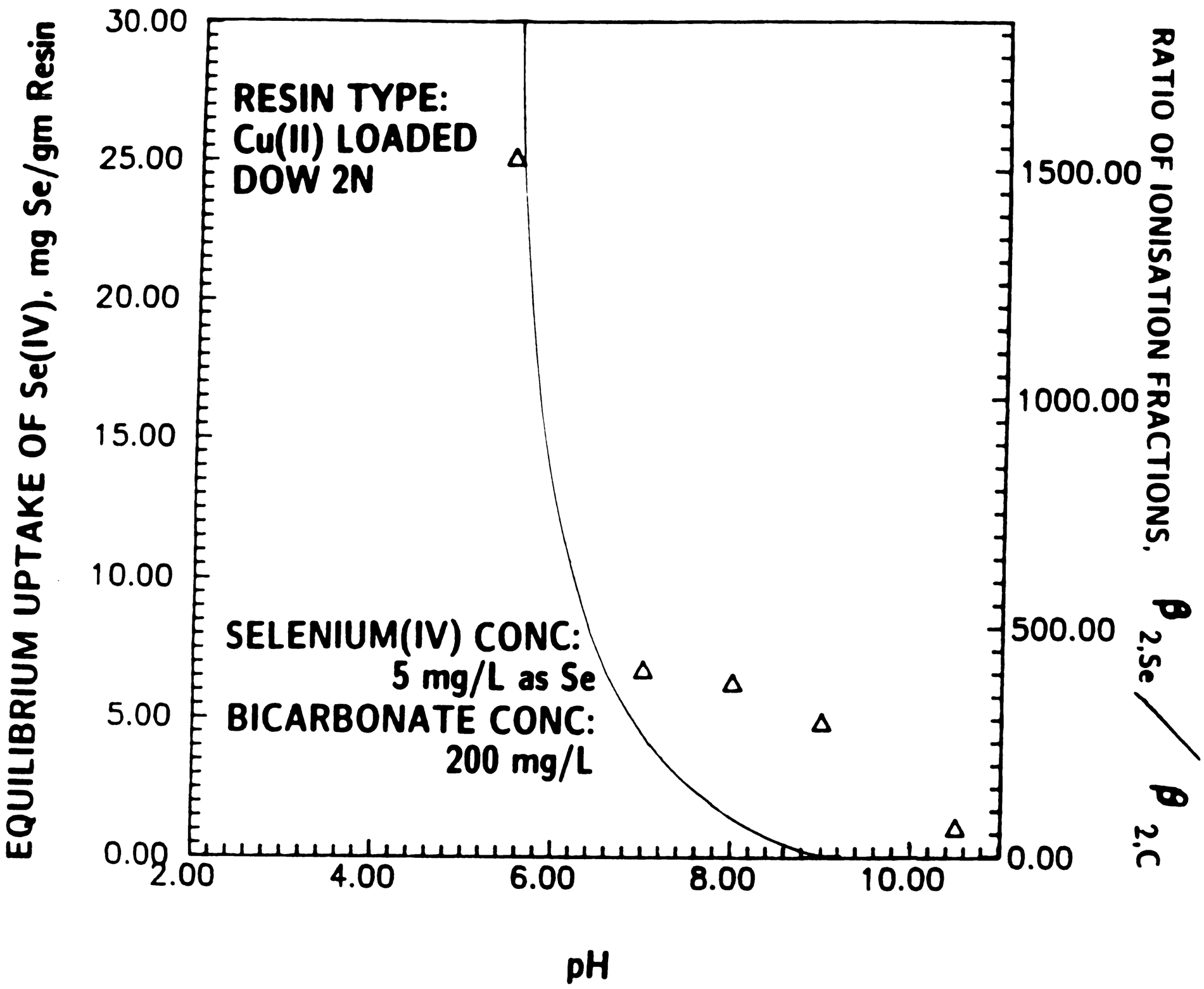


Figure 4-25: Uptake Of Selenite In The Presence Of Bicarbonate At Various pH Values

Serial No.	pH	Resin Phase Se(IV) Conc. q_{Se}, in mg Se/gm Resin	Resin Phase Carbon conc, q_C, in mg/gm Resin	Separation Factor, $\alpha_{Se/C} = \frac{q_{Se}\,[C]}{[Se]\,q_C}$.
1	5.5	25.06	188.91	1.05
2	7.0	6.74	278.86	0.19
3	8.0	6.27	194.90	0.25
4	9.0	4.87	165.75	0.23
5	10.5	1.10	219.00	0.04

Aqueous phase Se(IV) conc = 5 mg/L as Se
Total Bicarbonate conc = 200 mg/L
Total Carbon conc = 39.34 mg/L

Table 4-11: Effect Of pH On The Selenite-Bicarbonate Separation Factor For DOW 2N-Cu

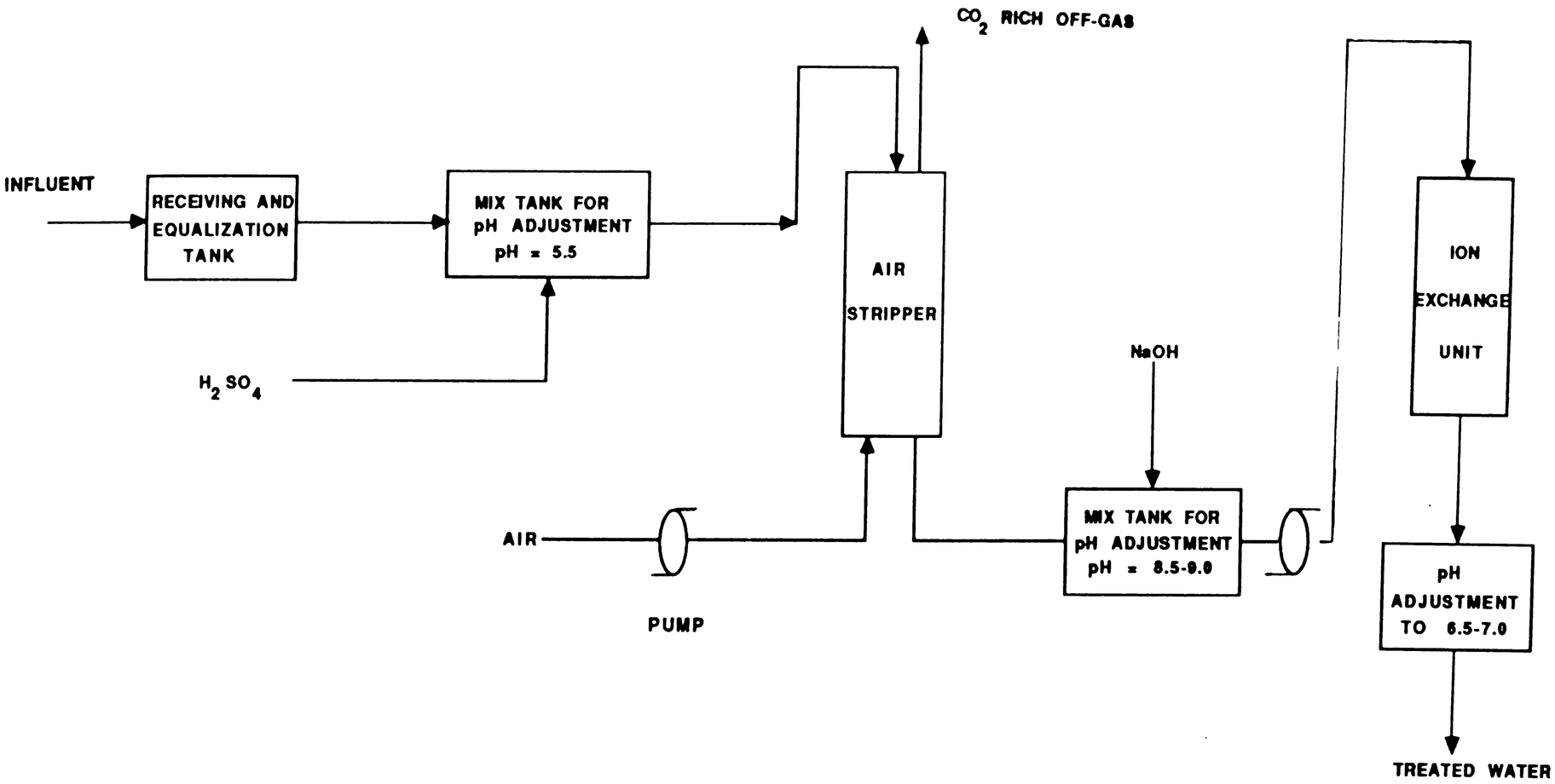


Figure 4-26: Proposed Method of Treatment of High Carbonate Waters With Arsenic And Selenium Contamination

conducted using DOW 3N-Cu. Figure 4-28 is the sulfide isotherm for this resin. The sulfide-sulfate separation factor, for DOW 3N-Cu, is presented in Table 4-13. The sulfide-sulfate separation factor for DOW 3N-Cu is lower than that determined for DOW 2N-Cu. This supports the observed lower anion exchange capacity of DOW 3N-Cu as compared to that of DOW 2N-Cu.

Thus any ligand, either organic or inorganic, which forms a copper compound with a high formation constant, could be a target for selective removal, using this method.

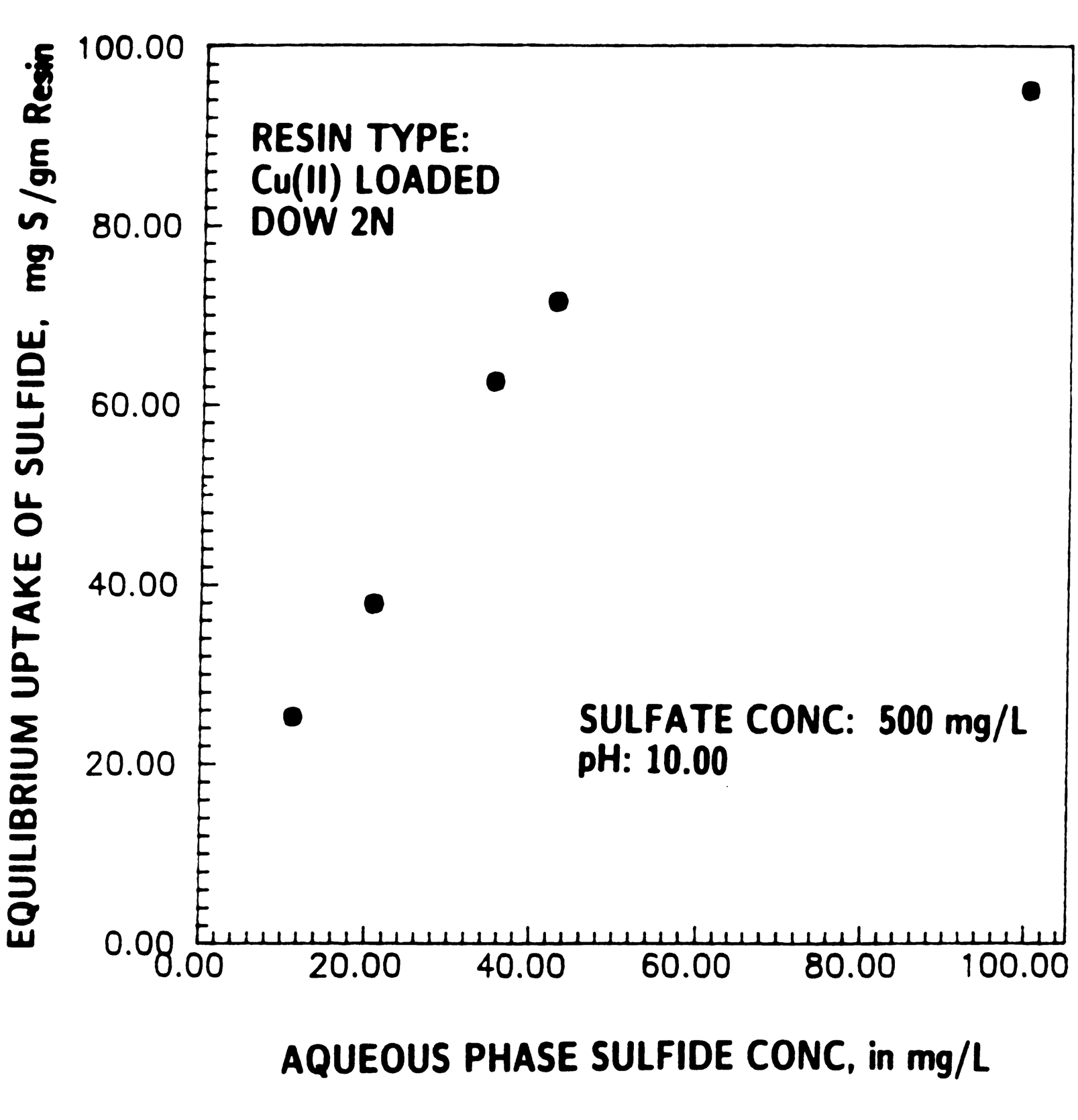


Figure 4-27: Sulfide-Sulfate Isotherm For DOW 2N-Cu At pH 10.00

Serial No.	Aqueous Phase Sulfide Conc, [S], in mg/L	Aqueous Phase Sulfate Conc, $[SO_4^{2-}]$, in mg/L	Resin Phase Sulfide Conc, q_S, in mg/gm Resin	Resin Phase Sulfate Conc, q_{SO_4}, in mg/gm Resin	Separation Factor, $\alpha_{S/SO_4} = \frac{q_S [SO_4]}{[S] q_{SO_4}}$
1	11.30	500	25.23	33.30	33.52
2	20.80	500	37.89	25.41	35.84
3	35.20	500	62.56	23.55	37.73
4	42.80	500	71.50	21.42	39.02
5	100.00	500	95.09	15.53	30.61

Table 4-12: Sulfide-Sulfate Separation Factor For DOW 2N-Cu At pH 10.00

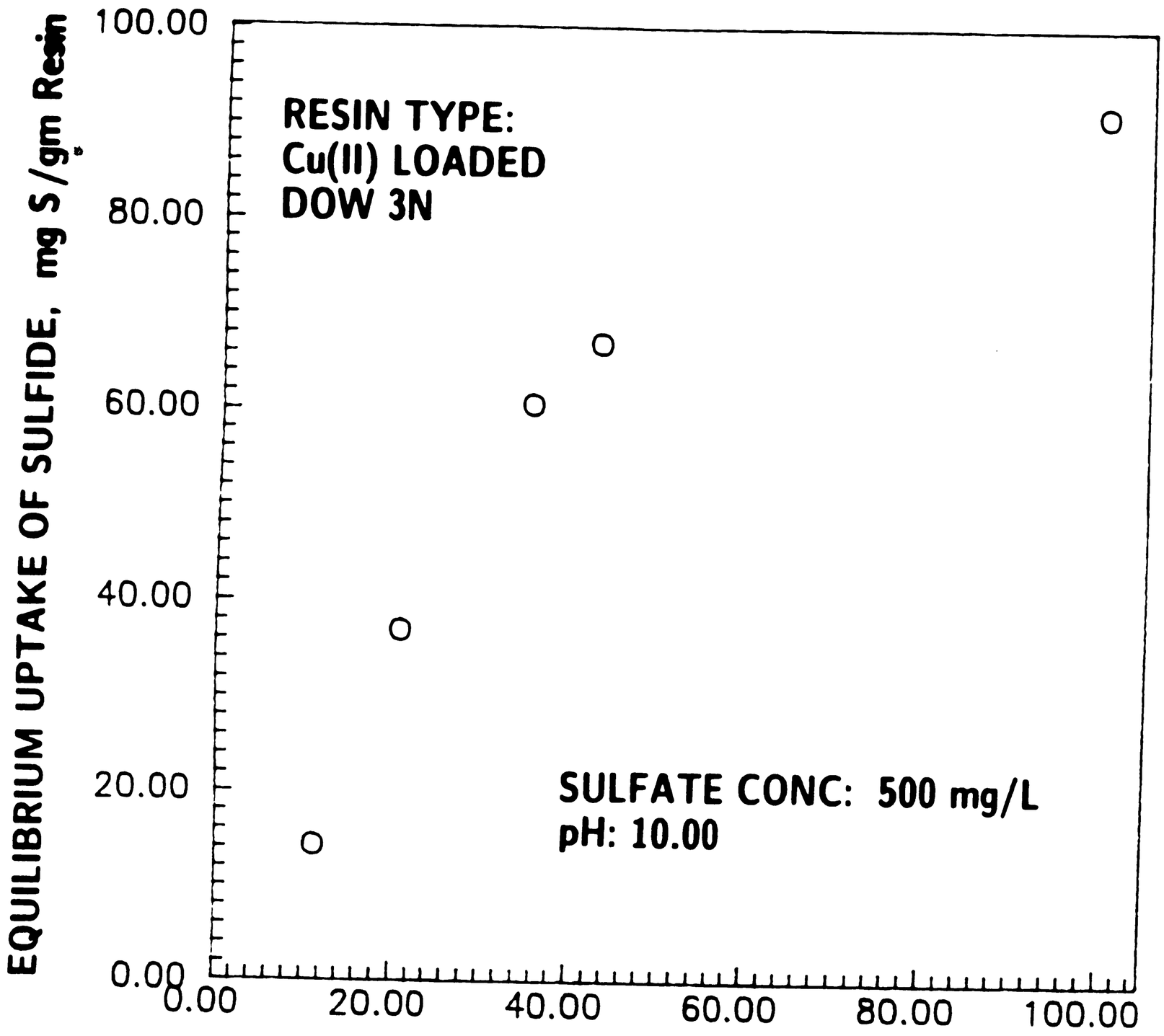


Figure 4-28: Sulfide-Sulfate Isotherm For DOW 3N-Cu At pH 10.00

Serial No.	Aqueous Phase Sulfide Conc, [S], in mg/L	Aqueous Phase Sulfate Conc, $[SO_4^{2-}]$, in mg/L	Resin Phase Sulfide Conc, q_S, in mg/gm Resin	Resin Phase Sulfate Conc, q_{SO_4}, in mg/gm Resin	Separation Factor, $\alpha_{S/SO_4} = \frac{q_S\,[SO_4]}{[S\,]\,q_{SO_4}}$
1	11.30	500	14.25	49.02	12.86
2	20.80	500	36.89	46.92	18.90
3	35.20	500	60.06	52.73	16.23
4	42.80	500	67.00	43.14	18.15
5	100.00	500	91.09	23.55	19.34

Table 4-13: Sulfide-Sulfate Separation Factor For DOW 3N-Cu At pH 10.00

Chapter 5
CONCLUSIONS AND REMARKS

5.1 BRIEF REVIEW OF THE CONDUCTED STUDY

Trace contamination of groundwaters by arsenic and selenium is fairly widespread. The removal of these species when present at low levels, in the presence of competing anions, is a separation problem that needs to be investigated. This would enable the efficient treatment of arsenic and selenium contaminated waters.

In this study, an attempt was made to improve the separation of arsenic(V) and selenium(IV) oxy-anions from the aqueous phase, in the presence of sulfate and chloride, using copper loaded chelating exchangers(with pyridine based functionalities).

DOW 2N and DOW 3N, in free base forms, were loaded with copper chloride and/or copper sulfate at pH 5.0. The modified synthetic sorbents were used to remove selenite and arsenate. The proposed mechanism of removal is ligand exchange induced sorption.

The removal of the arsenic(V) and selenium(IV) oxy-anions was enhanced by making use of the high formation constants(or low solubility products) of copper arsenate and copper selenite(Table 2-1). Sulfide removal was also investigated since cupric sulfide has a high formation constant, thus enabling increased separation of the sulfide anion in the presence of a high concentration of sulfate.

5.2 RESEARCH CONCLUSIONS

1. Selenite and arsenate selectivity, in the presence of sulfate and chloride, was increased by two orders of magnitude, over that of a strong base anion exchange resin, by using copper(II) loaded DOW 2N and DOW 3N(chelating polymers with a pyridine based functionality and a polystyrene matrix).

2. DOW 2N-Cu showed a higher selectivity for arsenate and selenite compared to DOW 3N-Cu.

3. The copper loaded chelating exchanger, DOW 2N-Cu, serves as an excellent sorbent for the arsenate and the selenite or biselenite ions, over a wide range of pH values.

4. The proposed mechanism, to explain this increased uptake, was anion exchange accompanied by Lewis acid-base interaction.

5. Uptake of the selenium(IV) oxy-anion, by DOW 2N-Cu, showed a consistent increase with increasing pH; this behavior was quantitatively explained using a mechanistic model.

6. Uptake of a species would depend on the formation constant of its copper compound. Thus, a stronger ligand would exhibit a higher selectivity. This was examined by studying the uptake of arsenate and selenite in the presence of bicarbonate. Bicarbonate would be a strong competing species because of the low solubility product(or high formation constant) of copper carbonate as compared to copper arsenate and copper selenite.

7. The uptake of arsenate in the presence of bicarbonate was low and followed the same trend as the ratio of the second ionization

fraction of arsenic acid to that of the second ionization fraction of carbonic acid. Similarly, uptake of selenite in the presence of bicarbonate was low, and followed the same trend as the ratio of the second ionization fraction of selenious acid to that of the second ionization fraction of carbonic acid. Please note that as the second ionization fraction of carbonic acid increases, the aqueous phase concentration of total carbon as carbonate also increases. Therefore, the competing ion concentration increases, reducing the uptake of arsenate and selenite.

8. Sulfide uptake by copper loaded DOW 2N was high, confirming the mechanism of ligand sorption accompanied by Lewis acid-base interaction. Please note that the formation constant of CuS is very high (K_{st}=1.58×10^{35}). Thus the Lewis Acid-Base interaction will also be very high, leading to high selectivity.

9. Once exhausted, the sorbents could be very efficiently regenerated, using a 2% ammonia solution and reused over a number of cycles.

5.3 REMARKS

1. The removal method investigated in this study could be useful for treating waters with trace concentrations of arsenate, selenite and sulfide. By concentrating these species on the solid phase, a large volume of contaminated water could be treated very efficiently. The contaminants can be immobilized without generation of sludge, a shortcoming of a conventional treatment technology, namely, coagulation.

2. Presence of bicarbonate is a deterrent for the applicablity of this

removal method. Some groundwaters are characterized by the presence of high concentrations of carbonate alkalinity. The use of this method would, therefore, require the pretreatment of the contaminated water for the removal of carbonate before the application of the process.

3. Further research and development would be necessary to determine the applicability of this process under a variety of groundwater conditions. Experiments need to be conducted to determine the kinetics of arsenic and selenium uptake by the synthetic sorbents.

4. Other species such as oxalate, phthalate, salicylate etc., which form copper complexes with high formation constants, could be targets for removal, using this method. Thus the tailored sorbent is very versatile and can also be used for the preferential removal of other trace species, which also act as strong ligands.

Appendix A

A.1 SORPTION ISOTHERMS

Ion exchangers can sorb solutes from solutions with which they are in contact. Sorption is a reversible phenomenon i.e., the sorbed solute can be removed from the ion exchanger by washing it with a suitable solution either acidic or alkaline.

Sorption isotherms describe in the form of functions or diagrams, at a given constant temperature, the dependence of the equilibrium concentration of the solute in the sorbent on its concentration in the external solution. The concentration in the sorbent is given per unit weight of blank sorbent.

The distribution coefficient of a solute is defined as the ratio of the concentrations of the solute in the sorbent and in the solution:

$$\lambda_i = \frac{\bar{m}_i}{m_i} \qquad A.1.1$$

$$\lambda'_i = \frac{\bar{C}_i}{C_i} \qquad A.1.2$$

Where,

λ_i = The molal distribution coefficient.

λ'_i = The molar distribution coefficient.

m_i = The concentration of solute i in millimoles per gram of solvent(molality).

C_i = The concentration of solute i in moles per liter of solvent(molarity).

Please note that the quantities with bars refer to the resin phase. $\bar{C}_i$ relates to the unit volume of the swollen sorbent. $\bar{m}_i$ is the concentration of solute i in millimoles per gram of swollen sorbent. The isotherms plotted in this study were molar isotherms and the sorbent was treated as a single quasi-

homogeneous phase[26]. However, all uptakes are reported in terms of unit weight(gram basis) of the sorbent(air-dried) used.

A.2 SEPARATION FACTOR

If two solutes are present, then the separation factor of one solute with respect to another, for a given resin can be defined as:

$$\alpha_{ij} = \frac{\lambda_i}{\lambda_j} \qquad A.2.1$$

Where, λ_i and λ_j are the distribution coefficients of the two species. The distribution coefficient for each solute(or species), as defined in Appendix A, being the ratio of the concentrations of the solute in the sorbent and in the solution.

If α_{ij} is greater than unity, it follows from equation A.2.1 that λ_i is greater than λ_j. This indicates that solute i is preferred over solute j, by the resin.

Appendix B

B.1 LOWER ARSENATE AND SELENITE SELECTIVITY OF DOW 3N-Cu AS COMPARED TO THAT OF DOW 2N-Cu

Since DOW 2N has one pyridine functionality, it can be represented by one molecule of pyridine for the purpose of discussion. Similarly, DOW 3N can be represented by two molecules of pyridine, as it has two pyridine functionalities. Uptake of the copper ion by DOW 3N may be represented by the following reaction,

$$2C_5H_5N+Cu^{2+}+2Cl^-=(C_5H_5N)_2Cu^{2+}(2Cl^-) \qquad B.1.1$$

Selenite interchange by this resin may be represented as follows,

$$(C_5H_5N)_2Cu^{2+}(2Cl^-)+SeO_3^{2-}=(C_5H_5N)_2Cu^{2+}(SeO_3^{2-})+2Cl^- \qquad B.1.2$$

Similarly, the reaction between DOW 2N and the copper ion may be represented by the following reaction,

$$C_5H_5N+Cu^{2+}+2Cl^-=(C_5H_5N)Cu^{2+}(2Cl^-) \qquad B.1.3$$

Selenite interchange by this resin may be represented as follows,

$$(C_5H_5N)Cu^{2+}(2Cl^-)+SeO_3^{2-}=(C_5H_5N)Cu^{2+}(SeO_3^{2-})+2Cl^- \qquad B.1.4$$

For the reaction represented by equation B.1.1, the logarithm of the equilibrium constant is 4.45. Similarly, for the copper uptake reaction for DOW 2N, the logarithm of the equilibrium constant is 2.56. The corresponding overall free energy change can be calculated using the expression,

$$\Delta G^o=-RTlnK \qquad B.1.5$$

Where, K is the value of the equilibrium constant.

By substituting the values of the respective equilibrium constants, the overall free energy changes for the reactions represented by equation B.1.1 and equation B.1.3, were determined to be -885.32 Kcal/mole and -557.44 Kcal/mole, using equation B.1.5 with an R value of 1.99 Kcal/mole and a T value of 298 K.

The overall free energy change can be given as the difference between the sum of the free energies of formation of the products and the sum of the free energies of formation of the reactants, as shown in equation B.1.6. As the free energies of formation of C_5H_5N (43.34 Kcal/mole)[18] and the cupric ion (15.66 Kcal/mole)[18] are known, the free energies of formation of the complexes, $(C_5H_5N)_2Cu^{2+}$ and $(C_5H_5N)Cu^{2+}$, could be determined by the stated rule and simple algebraic calculations. The values of the free energy of formation for these two compounds were determined to be -782.98 Kcal/mole and -498.44 Kcal/mole respectively.

$$\Delta G^o_{overall} = \Sigma \Delta G^o_f(products) - \Sigma \Delta G^o_f(reactants) \qquad B.1.6$$

A lower value of the free energy of formation for the copper form of DOW 3N, as compared to that for DOW 2N, indicates that it is more stable i.e., has a higher affinity. This was found to be true by experiment.

The overall free energy change, ΔG^o, for the reactions represented by equation B.1.2 and equation B.1.4, can also be expressed in terms of the selectivity coefficient, K_{se}, as follows:

$$\Delta G^o = -RTlnK_{se} \qquad B.1.7$$

Since the proposed mechanism of anion uptake by these resins is ion exchange accompanied by Lewis Acid-Base interaction, presence of a greater number of unsatisfied coordinate valences of the copper ion should result in higher anion(ligand) selectivity. As the copper ion in DOW 3N is chelated to three nitrogen atoms (two pyridine nitrogens and one tertiary nitrogen) it should have a lower coordination valence than the copper ion in DOW 2N (where it is chelated to one pyridine nitrogen and one secondary amine nitrogen). Therefore, the complex between the resin bound cupric ion and the selenite ion will be formed more readily in the case of DOW 2N. This would imply a lower free energy of formation for the compound.

Thus the overall free energy change for the reaction, represented by equation B.1.4, will be more negative compared to that for the reaction represented by equation B.1.2. Using equation B.1.7, this would imply a higher value of K_{se} for DOW 2N-Cu as compared to DOW 3N-Cu.

Although many simplifying assumptions were made, such as assumption of an identical matrix and assumption of interaction of the copper ion with only the pyridine nitrogens, lower selenite and arsenate selectivity, in the case of DOW 3N-Cu could be explained.

Appendix C

C.1 COMPUTATION OF IONIZATION FRACTIONS

Arsenic acid, or H_3AsO_4, is a triprotic acid and therefore has three ionization constants as shown below.

$$H_3AsO_4 = H^+ + H_2AsO_4^-$$

$$H_2AsO_4^- = H^+ + HAsO_4^{2-}$$

$$HAsO_4^{2-} = H^+ + AsO_4^{3-}$$

For the aforementioned reactions, the pK values are 2.5, 6.77 and 11.5 respectively. $\beta_{1,As}$ corresponds to the fraction of total arsenic present as $H_2AsO_4^-$. Similarly, $\beta_{2,As}$ and $\beta_{3,As}$ represent the fractions of total arsenic present as $HAsO_4^{2-}$ and AsO_4^{3-}.

Carbonic acid, or H_2CO_3, is a diprotic acid and has two ionization constants. These correspond to the following reactions,

$$H_2CO_3 = H^+ + HCO_3^-$$

$$HCO_3^- = H^+ + CO_3^{2-}$$

The pK values for the stated reactions are 6.3 and 10.3 respectively. $\beta_{1,C}$ corresponds to the fraction of total carbon present as HCO_3^- and $\beta_{2,C}$ to the fraction of total carbon present as CO_3^{2-}.

Selenious acid, or H_2SeO_3, is a diprotic acid and has two ionization constants. These correspond to the following reactions,

$$H_2SeO_3 = HSeO_3^- + H^+$$

$$HSeO_3^- = SeO_3^{2-} + H^+$$

The pK values for the stated reactions are 2.4 and 7.9 respectively. $\beta_{1,Se}$ and $\beta_{2,Se}$ correspond to the fraction of total selenium present as $HSeO_3^-$ and SeO_3^{2-}.

For a general diprotic acid, H_2A, the concentrations of the species, HA^-

and A^{2-}, are given by the following expressions:

$$[HA^-] = C_{T,A}\left(\frac{1}{([H^+]/K_{a,1}) + 1 + (K_{a,2}/[H^+])}\right) \qquad C.1.1$$

$$[A^{2-}] = C_{T,A}\left(\frac{1}{([H^+]^2/K_{a,1}K_{a,2}) + ([H^+]/K_{a,2}) + 1}\right) \qquad C.1.2$$

Where $K_{a,1}$ and $K_{a,2}$ stand for the first and the second ionization constants of the acid and $C_{T,A}$ is the total concentration of the diprotic acid.

Similarly, for a general triprotic acid, H_3A, the concentrations of the species, H_2A^-, HA^{2-} and A^{3-}, are given by the following expressions:

$$[H_2A^-] = C_{T,A}\left(\frac{1}{([H^+]/K_{a,1}) + 1 + (K_{a,2}/[H^+]) + (K_{a,2}K_{a,3}/[H^+]^2)}\right) \qquad C.1.3$$

$$[HA^{2-}] = C_{T,A}\left(\frac{1}{([H^+]^2/K_{a,1}K_{a,2}) + ([H^+]/K_{a,2}) + 1 + (K_{a,3}/[H^+])}\right) \qquad C.1.4$$

$$[A^{3-}] = C_{T,A}\left(\frac{1}{([H^+]^3/K_{a,1}K_{a,2}K_{a,3}) + ([H^+]^2/K_{a,2}K_{a,3}) + ([H^+]/K_{a,3}) + 1}\right) \qquad C.1.5$$

Where, $K_{a,1}$, $K_{a,2}$ and $K_{a,3}$ stand for the first, second and third ionization constants, respectively, for the acid H_3A. $C_{T,A}$ is the total concentration of the triprotic acid. Table C-1 gives the second ionization fraction for arsenic acid and carbonic acid at various pH values. These values were used to generate the solid line in Figure 4-24. Similarly, Table C-2 gives the second ionization fraction for selenious acid and carbonic acid at various pH values. These values were used to generate the solid line in Figure 4-25.

Serial No.	pH	$\beta_{2,As}$	$\beta_{2,C}$	$\beta_{2,As} / \beta_{2,C}$
1	6.0	0.145	$1.673X10^{-5}$	8667.07
2	7.0	0.629	$4.176X10^{-4}$	1506.23
3	8.2	0.964	$7.784X10^{-3}$	123.85
4	9.0	0.992	$4.764X10^{-2}$	20.83
5	10.0	0.976	0.334	2.92

Table C-1: Second Ionization Fraction For Arsenic Acid At Different pH Values

Serial No.	pH	$\beta_{2,Se}$	$\beta_{2,C}$	$\beta_{2,Se} / \beta_{2,C}$
1	5.5	$3.96X10^{-3}$	$2.17X10^{-6}$	1826.37
2	7.0	0.112	$4.18X10^{-4}$	267.69
3	8.0	0.557	$4.89X10^{-3}$	113.97
4	9.0	0.926	0.048	19.45
5	10.5	0.998	0.613	1.63

Table C-2: Second Ionization Fraction For Selenious Acid At Different pH Values

It was attempted to predict the arsenate uptake using the ratio of $\beta_{3,As}$ to that of $\beta_{2,C}$. Table C-3 tabulates the value of the ratio at different pH values. From Figure C-1, it can be seen that this ratio does not follow the same trend as the arsenate uptake. The variation of this ratio with pH, is indicated by a solid line in the Figure C-1.

Serial No.	pH	$\beta_{3,As}$	$\beta_{2,C}$	$\beta_{3,As} / \beta_{2,C}$
1	6.0	7.326×10^{-6}	1.673×10^{-5}	0.433
2	7.0	1.581×10^{-5}	4.176×10^{-4}	0.038
3	8.2	3.837×10^{-4}	7.784×10^{-3}	0.049
4	9.0	2.491×10^{-3}	4.764×10^{-2}	0.052
5	10.0	2.449×10^{-2}	0.334	0.073

Table C-3: Third ionization fraction For Arsenic Acid At Different pH Values

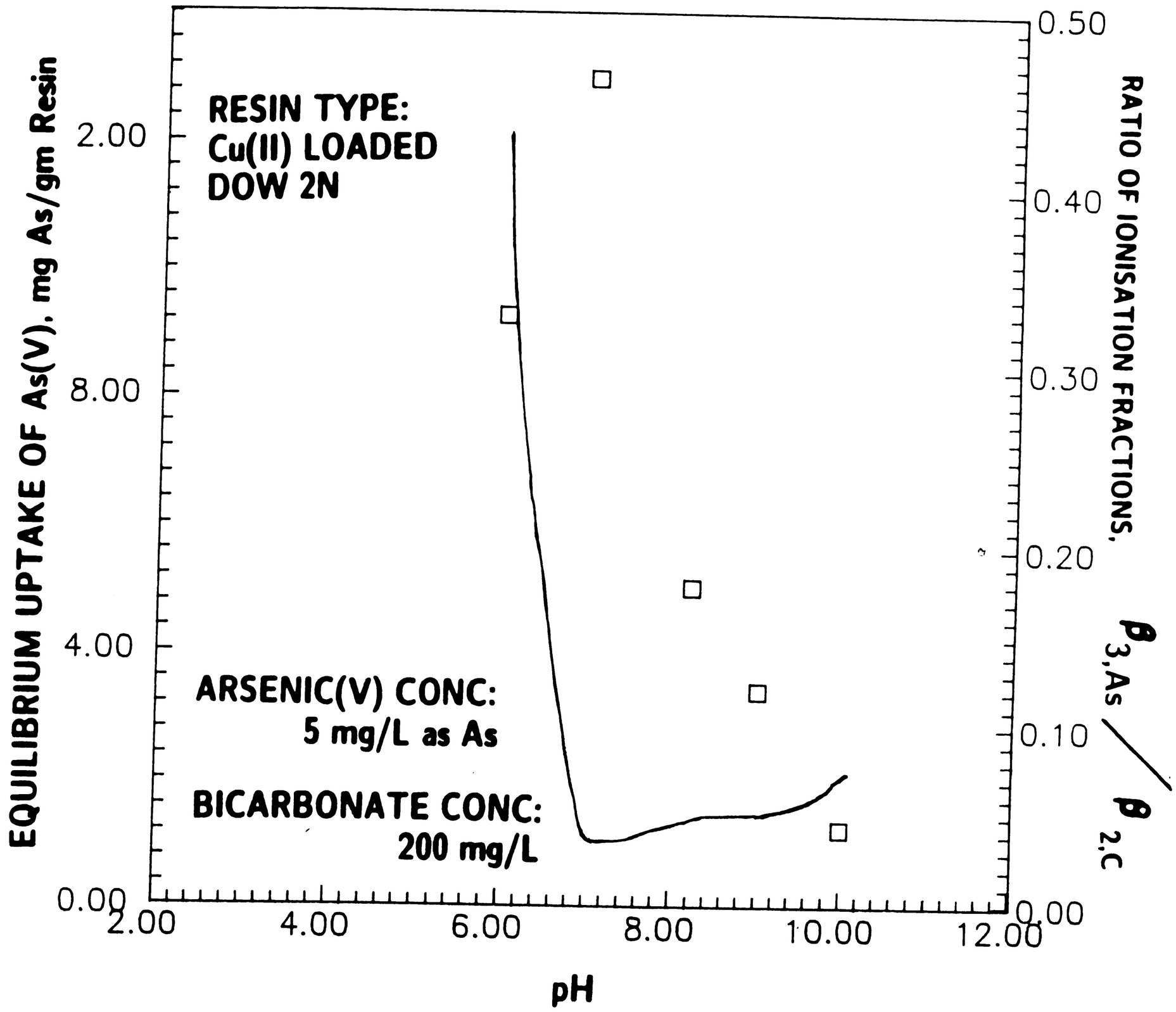


Figure C-1: Uptake Of Arsenate In The Presence Of Bicarbonate At Various pH values

Appendix D

D.1 THEORETICAL COMPUTATION OF SELENIUM UPTAKE

The total selenium uptake by the resin can be given by the following expression:

$$q_{Se} = q_I + q_{II} \qquad D.1.1$$

For the sake of simplicity, $q_{HSeO_3^-}$ will be referred to as q_I, and $q_{SeO_3^{2-}}$ as q_{II}. q_I and q_{II} can be computed using equation 4.1.8 and equation 4.1.9 respectively . The values of K_I and K_{II}, as indicated in Table 4-5, are 76.621 and 20.114 respectively. The total aqueous phase selenium concentration, $C_{T,Se}$ was taken to be 2.53×10^{-2} mmole/L. The aqueous phase sulfate concentration was taken to be 2.604 mmole/L. Since these were the concentrations used in the experiment. Using equation 4.1.8 and equation 4.1.9 and the stated values of total selenium and sulfate concentrations, and K_I and K_{II}, q_I and q_{II} can be computed using the following expressions:

$$q_I = 29.424\, q_{SO_4}\, C_{Se1}^2 \qquad D.1.2$$

$$q_{II} = 7.724\, q_{SO_4}\, C_{Se2} \qquad D.1.3$$

From the experimental data, it was found that the quantity, $(q_{Se} + q_{SO_4})$, was fairly constant and had a value of 0.9768 mmole/gm Resin. Therefore, the following expressions were used to calculate q_I and q_{II}:

$$q_I = 29.424\, C_{Se1}^2 [0.9768 - q_I] \qquad D.1.4$$

$$q_{II} = 7.724\, C_{Se2}\, [0.9768 - q_{II}] \qquad D.1.5$$

The calculations are tabulated in Table D-1.

Serial No.	pH	C_{Se1} (mmole/L)	C_{Se2} (mmole/L)	q_I mmole/gm Resin	q_{II} mmole/gm Resin
1	3.0	2.022×10^{-2}	—	1.161×10^{-2}	—
2	4.0	2.467×10^{-2}	—	1.718×10^{-2}	—
3	5.0	2.520×10^{-2}	—	1.792×10^{-2}	—
4	6.0	2.498×10^{-2}	—	1.762×10^{-2}	—
5	6.5	2.433×10^{-2}	9.70×10^{-4}	1.672×10^{-2}	7.264×10^{-3}
6	7.5	1.810×10^{-2}	7.20×10^{-3}	9.320×10^{-3}	5.146×10^{-2}
7	8.0	1.120×10^{-2}	1.410×10^{-2}	3.68×10^{-3}	9.590×10^{-2}
8	9.0	1.861×10^{-3}	2.34×10^{-2}	—	1.497×10^{-1}
9	10.0	—	2.530×10^{-2}	—	1.596×10^{-1}
10	11.0	—	2.530×10^{-2}	—	1.596×10^{-1}

$q_{Se} = q_I + q_{II}$

Total resin phase selenium conc, in mmole/gm = q_{Se}

Table D-1: Theoretical Uptake Values For Selenium

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